## THE ANALYST

# PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

AN Ordinary Meeting of the Society was held on Wednesday, October 1st, at the Chemical Society's Rooms, Burlington House. The President, Mr. G. Rudd Thompson, F.I.C., was in the chair.

Certificates were read for the first time in favour of:—Messrs. Arthur Cecil Brooks, A.I.C.; William Donovan, M.Sc.; Albert George Flower, B.Sc.; Clifford Hollingsworth, F.I.C.; George Marshall Norman, B.Sc., A.R.C.S., F.I.C.; Charles Edward Sage, F.I.C.; Percy Frank Spendlove, B.Sc., A.R.C.S., A.I.C.; Charles William Spiers, M.Sc., A.I.C.; Leslie Hubert Trace, B.Sc., A.I.C.; and James Rawson Walmsley.

Certificates were read for the second time in favour of Messrs. Johan Ernst Nyrop, and Clifford Padgett Thorpe, B.Sc.

Messrs. G. W. Clough, D.Sc., J. P. Shenton, F.I.C., and W. S. Wood were elected members of the Society.

The following papers were read:—"The Estimation of Coconut Oil and Butter Fat in Margarine," by G. D. Elsdon and P. Smith; "A Preliminary Note on the Composition of the Fat of Goat's Butter," by F. Knowles and J. C. Urquhart; "The Quantitative Estimation of the Degree of Hydrolysis of Gallotannin by Tannase," by Miss W. N. Nicholson and D. Rhind; "The Pemberton-Neumann Method for the Estimation of Phosphorus," by Miss M. B. Richards and W. Godden and "Application of 'Formol Titration' to the Kjeldahl Method of Estimating Nitrogen," by W. S. Shaw.

## Death.

It is with deep regret that we have to record the death, on September 9, of Mr. Otto Hehner, Past President, and one of the earliest members of our Society. An obituary notice will be published in the next issue.

## The Recognition of Hydrogenated Oils.

BY K. A. WILLIAMS, B.Sc., AND E. R. BOLTON, F.I.C.

(Read at the Meeting, May 7, 1924.)

THE test most widely applied for the detection of hydrogenated oils is based on the presence of traces of nickel in the oil, nickel being the catalyst used almost universally for the commercial hydrogenation of oils. The evidence given by this test is confirmed by the use of certain tests of minor importance and of doubtful reliability, the best known of which depends on the microscopic examination of the crystals deposited by the fat from its solution in ether.

The search for traces of catalyst is of assistance only when a positive result is obtained, since a negative result does not exclude the possibility of the presence of hydrogenated oil, and is of less value now than formerly owing to the greater skill of the manufacturer in removing nickel from his hardened product. The trace of nickel which remains nowadays in these products is usually so small as to necessitate the use of a larger quantity of fat for the test than is usually available.

ISO-OLEIC ACID.—The authors have taken advantage, for the detection of hydrogenated oils, of a discovery first mentioned in 1913 by Lewkowitsch\* and investigated by Moore.<sup>†</sup> These workers have pointed out that, during the course of hydrogenation of oils, there is formed an acid which had not previously been observed in oils derived from natural sources. This acid, which consists of one or more isomers of oleic acid, was termed iso-oleic acid, even though that name is used for other mixtures of oleic acid isomers.

The presence, then, of this new iso-oleic acid in edible fats in any quantity is proof of the presence of hydrogenated oils. It should be noticed, however, that Twitchell<sup>‡</sup> states that he has found iso-oleic acid to be present to a limited extent (about one per cent.) in beef tallow. This appears to be the sole exception to the rule that iso-oleic acid does not occur in nature.

*Iso-oleic acid* appears to consist mainly of elaidic acid and contains probably certain other isomers of oleic acid, notably the 11.12 acid. It is a solid mixture at ordinary temperatures and has an iodine value of 90.

Its characteristic property is that, abhough unsaturated, it forms a lead salt nearly insoluble in most of the commonly employed organic solvents, *e.g.* ether, alcohol, benzene. In this it resembles the saturated acids, which also form insoluble lead salts, and differs from the other unsaturated acids whose lead salts are (except in the case of erucic acid and possibly of elaeostearic acid) soluble in these solvents.

\* Lewkowitsch, Oils, Fats and Waxes, I., 192 (5th Ed.).

† Moore, J. Soc. Chem. Ind., 1919, 38, 320T.

‡ J. Ind. Eng. Chem., 1921, 13, 806.

#### WILLIAMS AND BOLTON: THE RECOGNITION OF HYDROGENATED OILS 461

The estimation of iso-oleic acid is based on this property. The lead salts from a few grms. of the fat are formed quantitatively, and from these the lead salts of the unsaturated acids (*e.g.* oleic, linolic) are separated by extraction with one of the above-named solvents. The insoluble lead salts of the saturated acids and iso-oleic acid are washed as free as possible from the soluble lead salts. The acids are liberated from either or both fractions in ether; the ether is distilled off, and the acids are dried and weighed.

If the oil contains no hydrogenated oil the iodine value of the solid fraction will be not greater than 5 units (due to incomplete removal of unsaturated liquid acids in washing). If hydrogenated fat be present to any extent, this iodine value will be higher owing to the presence of iso-oleic acid, the content of which is calculated from this iodine value.

Allowing 5 units of iodine value in the solid fraction due to incomplete washing, the proportion of iso-oleic acid in the total fatty acids from the oil is given by the expression

Percentage of iso-oleic acid  $= \frac{95}{100} \times S \times \frac{I-5}{90}$ .

Where S = percentage of solid fraction obtained, and I = its iodine value.

The liquid fraction in each case contains the unsaponifiable matter of the fat. In a complete determination of the composition of the fatty acids this would have to be estimated and an allowance made for its effect on the iodine value of this fraction.\* The solid fraction will be free from unsaponifiable matter, and, if only the proportion of iso-oleic acid is to be estimated, no correction is necessary.

SEPARATION OF SOLID AND LIQUID FATTY ACIDS.—Of the various methods of separation of solid and liquid fatty acids which have been proposed, the authors recommend as most satisfactory, either

- (1) the lead salt and ether method of Gusserow-Varrentrapp; or
- (2) the alcohol method of Twitchell.

Details of the procedure to be followed in the first of these may be found in most text books on oil analysis.<sup>†</sup> Details of the second are to be found in Twitchell's original paper.<sup>‡</sup>

Other methods the efficiency of which the authors have investigated include

(A) Separation of the thallium salts with water containing a small quantity of alcohol.§

\* Such determinations are described in full in "Fats, Natural and Synthetic," Middleton and Barry, p. 114.

† E.g. Bolton and Revis, Fatty Foods, p. 31.

± J. Ind. Eng. Chem., 1921, 13, 806, abstracted in ANALYST, 1921, 46, 466.

§ Meigen and Neuberger, Chem. Umschau, 1922, 29, 337.

#### (B) The separation of lead salts with

- (a) Petroleum spirit.
- (b) A mixture of 1 volume of petroleum spirit with 1 volume of methylated ether.

Using the first of these methods (A) and adhering to the authors' details, we have been quite unable to obtain an efficient separation. (Cf. ANALYST, 1924, 448.)



The results of separations by the other methods mentioned above on a typical hydrogenated cotton seed oil are shown in the table. It will be noticed that separation with mixed petroleum spirit and methylated ether gives results in close agreement with those obtained by the lead salt with ether or alcohol processes. Separation with petroleum spirit leads to erroneous results for the iso-olcic acid (and the olcic acid) content, the apparent iso-olcic acid content being much higher than that obtained by the use of any other solvent, and furthermore, not being constant, but varying with the time for which the lead salts are left in contact with the solvent. This variation is shown in Figure I. The shape of this curve appears to indicate that lead oleate crystallises slowly from petroleum spirit, even from dilute solution.



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	<b>m</b> : <b>f</b> , ,	COMPOSITION.							
Solvent used for separation of Lead Salts. Methylated ether	of Lead Salts and Solvent.	Linolic Acid. 6·1	Oleic Acid. 40·0	Iso-oleic Acid. 24.8	Saturated Acids. 29·1				
Alcohol	<u> </u>	$6 \cdot 2$	40.8	$23 \cdot 8$	$29 \cdot 2$				
1 part meth. ether 1 part petroleum spirit		5.5	<b>43</b> ·1	22.9	28.5				
Petroleum spirit	$\left\{\begin{array}{ll}18 \text{ hours}\\1\frac{1}{2} \text{ days}\\5\frac{1}{2} \text{ days}\\9 \text{ days}\end{array}\right.$	$5 \cdot 2 \\ 5 \cdot 6 \\ 5 \cdot 7 \\ 5 \cdot 2$	33.0 31.4 25.9 21.7	$34 \cdot 2 \\ 35 \cdot 2 \\ 40 \cdot 0 \\ 45 \cdot 0$	$27.6 \\ 27.6 \\ 29.4 \\ 28.1$				

HYDROGENATED COTTON SEED OIL.

APPROXIMATE ESTIMATION OF HYDROGENATED OIL.—As a guide to the approximate estimation of hydrogenated oil in mixtures we have prepared the curves in Fig. 2 which show the average compositions of the fatty acids from various hydrogenated vegetable oils at different stages of hydrogenation, the exact stage being shown by the iodine value of the fat.

These curves illustrate the well-known resemblance in composition between fats obtained by hydrogenation of different vegetable oils, and the consequent difficulty of determining the source of the hardened product.

Most commercial hydrogenated oils used in edible products have iodine values lying between 50 and 70 units and contain from 30 per cent. to 35 per cent. of iso-oleic acid, from which figures the approximate proportion of hydrogenated oil in the mixture may be deduced.

A drastic change in the composition of hydrogenated oils has recently resulted from a modification of the methods employed, by the introduction of a continuous process, whereby a flow of oil passes through a relatively large mass of catalyst.\* The process can be operated so as to produce

(a) the normal proportion of iso-oleic acid in the product,

or (b) a reduced amount.

It will be obvious that the control of the proportion of iso-oleic acid on a commercial scale militates against the accuracy of the deductions made from the process the use of which the authors have suggested, with the result that in cases where the method of hydrogenation employed is unknown the proportion of hydrogenated oil may be largely over-estimated. The value of the process for the actual detection of hydrogenated oil remains, however, unaltered.

#### DISCUSSION.

Mr. W. H. SIMMONS, referring to Mr. Williams' remark that iso-oleic acid was discovered in 1913, said he thought that a perusal of the literature would probably prove that it had been discovered fifty or more years earlier. If, however, he was referring to a different isomer it was a pity the same name should be employed for two.

\* Eng. Pat. 162370, E. R. Bolton.

#### STEUART: THE CITRIC ACID CONTENT OF MILK POWDER

Mr. E. J. LUSH suggested that the neutralisation value of the solid acids would be of assistance in deciding as to the oil from which a hydrogenated oil had been produced, as from this figure the proportion of palmitic acid in the oil could be obtained, this acid being one which remained constant in quantity during hydrogenation. The 50 iodine value point was interesting because it was the range used for soap and margarine. The composition chart gave the impression that when one got to an iodine value of 50 it was immaterial what oil one started from. He thought it would be very interesting to see a similar composition chart in which the melting point instead of the iodine value was used to denote degree of hydrogenation, because this would bring into play that important factor the tribasic nature of glycerin. Such a chart might bring out differences between different oils.

Mr. C. L. HINTON enquired whether corrections had to be made for the unsaturated acids not washed out from the saturated acids in the separation; and whether some corrections would not have to be made for unsaponifiable matter present in the fat.

Mr. K. A. WILLIAMS, in reply, said that, with regard to the corrections that would be applied normally to the iodine value, the iodine value of the solid acids obtained from an oil containing no iso-oleic was usually about 5, and it could be assumed that the unsaturated acids present as impurities in the solid acids would increase the iodine value of these by 5 units—*i.e.*, the iodine value obtained could be regarded as 5 units too high and be adjusted accordingly.

As to Mr. Lush's remarks he did not think that the neutralisation value of the solid fatty acids would help much, in that the solid acids of many of the oils were mostly palmitic acid, and the differences in the content of this acid in various liquid oils were not marked.

Regarding the question of composition and the tribasic nature of glycerin, there was scope for much work in this direction; the authors had not touched upon that point in the paper.

## The Citric Acid Content of Milk Powder.

BY DAN. W. STEUART, B.Sc. (Agr.).

(Read at the Meeting, May 7, 1924.)

VARIOUS estimations of the citric acid content of fresh milk which have been published indicate that from 0.15 to 0.2 per cent. is present. This would be concentrated some three-fold in the case of sweetened condensed milks, eight-fold in the case of full-cream milk powders, and eleven-fold in the case of skim-milk powders. The amount of citric acid in milk powder must then be quite considerable.

Two methods for estimating citric acid were tried, *viz.* by weighing it as pentabromacetone, and by weighing it as the double salt of mercury acetone dicarboxylate with basic mercury sulphate.

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A. STAHRE'S PENTABROMACETONE METHOD.\*—Five grms. of the milk powder were dissolved in 45 c.c. of warm water, 10 cc. of 50 per cent. sulphuric acid added, and then 2 c.c. of 40 per cent. potassium bromide solution, and 20 c.c. of 10 per cent. phosphotungstic acid. After mixing, the whole was filtered, and the filter was washed with water till the filtrate measured 150 c.c. To this was added excess of fresh bromine water, and the temperature raised to  $50^{\circ}$  C. for 5 minutes. Then potassium permanganate solution (5 per cent.) was added, drop by drop, slowly, so that the temperature did not rise appreciably, and with stirring all the time, till a brown precipitate formed. Ferrous sulphate solution was now stirred in till the precipitate was decolorised. After standing overnight, the precipitate was collected on a prepared asbestos Gooch filter, washed with water acidified with sulphuric acid, and with distilled water, and then dried for 24 hours in a vacuum desiccator over sulphuric acid.

> Weight of precipitate  $\times 0.424$  = Anhydrous citric acid. ,, ,, ,,  $\times 0.464$  = Crystalline citric acid.

The following percentages of anhydrous citric acid in milk powders were obtained.

Full cream, per cent.:

$$1\cdot 11, \ 1\cdot 13, \ 1\cdot 21, \ 0\cdot 98, \ 1\cdot 30, \ 1\cdot 13, \ 0\cdot 97, \ 1\cdot 31, \ 0\cdot 96, \ 1\cdot 31, \ 1\cdot 21, \ 1\cdot 27, \ 1\cdot 17.$$

Skim-milk, per cent.:

 $\begin{array}{c} 1 \cdot 48 \\ 1 \cdot 50 \end{array} \} \text{ av. } 1 \cdot 49; \begin{array}{c} 1 \cdot 65 \\ 1 \cdot 80 \end{array} \} \text{ av. } 1 \cdot 72; \begin{array}{c} 1 \cdot 37 \\ 1 \cdot 58 \end{array} \} \text{ av. } 1 \cdot 47; 1 \cdot 55, 1 \cdot 73, 1 \cdot 46, 1 \cdot 68, 1 \cdot 39, \\ 1 \cdot 60, 1 \cdot 47, 1 \cdot 60. \end{array}$ 

The precipitate consisted of practically pure penta-bromacetone. A trace of brominated protein was removed by dissolving the substance in ether and filtering the solution. The recovered compound melted at 72 to  $75^{\circ}$  C. and yielded 88.0 per cent. of bromine (by Stephanow's method followed by titration by Volhard's method).

Pure crystalline citric acid was then used for a series of estimations after verifying the purity by the neutralisation value and the moisture content. Seven estimations, in which 0.1 grm. in 150 c.c. of water was used, gave from 90.0 to 93.5 per cent. (av. 92 per cent.) of the theoretical yield of pentabromacetone. The low results were attributed to over-oxidation.

B. BEAU'S MERCURY SULPHATE METHOD.<sup>†</sup>—In this case 5 grms. of milk powder were transferred to a 200 c.c. flask with 100 c.c. of water. Then 50 c.c. of mercury sulphate reagent were added and a little 10 per cent. phosphotungstic acid. After mixing, the solution was made up to the mark and filtered. To 100 c.c. of the filtrate at the boiling point, 1 per cent. potassium permanganate solution was added, drop by drop, with constant stirring, till a brown precipitate settled down. The liquid was boiled again, and a little hydrogen peroxide solution

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<sup>\*</sup> Abstracts in ANALYST, 1922, 47, 24; 1916, 41, 378.

<sup>+</sup> See Local Govt. reports on Milk Powders, 1920; also Barthel's "Milk and Dairy Products."

stirred in till the precipitate looked clean. The precipitate was then collected on a Gooch filter, washed with water and dried at  $105^{\circ}$  C. for 2 hours.

Weight of precipitate  $\times 0.271$  = Anhydrous citric acid. ,, ,, ,,  $\times 0.296$  = Crystalline citric acid.

The usual method of preparing the mercury reagent is as follows:—To 50 grms. of red oxide of mercury and 400 to 500 c.c. of water in a litre flask add sufficient (about 75 c.c.) concentrated sulphuric acid, gradually, to dissolve all the powder. Make up the solution to 1000 c.c., boil and filter. This solution gave too high results when pure citric acid was used. The Local Govt. Report states that 5 c.c. of the reagent should require 7 to 8 c.c. of N sodium hydroxide solution before giving a permanent turbidity. The reagent was thus considered to be insufficiently acid. When this was put right the results obtained with pure citric acid were low. The following percentages of anhydrous citric acid in milk powders were obtained:

Full cream, 1.21, 1.13, 0.89, 1.20,  $\begin{pmatrix} 1.42 \\ 1.44 \end{pmatrix}$  av. 1.43. Skim milk, 1.42.

The precipitate in this case was filtered off with greater difficulty than in the case of the former method.

SUMMARY.—The amount of citric acid in milk powder is quite considerable, being equal roughly to one-fifth of the ash. A sample of fresh milk (April) gave 0.158 per cent. of anhydrous citric acid. The average figure obtained with full cream milk powders was 1.16 per cent., and with skim milk powders 1.55 per cent. In each case this would be equal to 0.144 per cent. in the original milk. These figures are on the low side.

## An Apparently Specific Test for Tannins.

By ALAN H. WARE.

To the present writer the term "tannin" connotes a complex phenol, or phenolcarboxylic acid, which is astringent to the taste, water-soluble, will convert hide or skin into leather, and form an ink with soluble simple iron salts. The goldbeater's skin test for tannins (ANALYST, 1924, 25) has a special value in that it recognises, and combines in one concrete form both the chemical reactions named in the above definition. For research work, and for use in checking the validity of any new test, either the goldbeater's skin test or some similar test, or set of tests, will always be necessary.

As a routine test, however, the goldbeater's skin test suffers from the following disadvantages, viz. (1) That it takes fully an hour to complete, and this is a very

long time for a routine qualitative test. (2) That, whilst a negative result undoubtedly implies the absence of tannin, a positive result, with respect to ironcoloration, does not *necessarily* imply the presence of tannin; for certain other substances give iron-colorations on the skin closely resembling the results yielded by weak tannin extractives. Hitherto no single test has been published for tannins *as a class*, which answers the several and combined requirements of being really specific, suitable for rapid routine work, and capable of giving obvious and emphatic results. The writer believes that the test here described will fulfil all these desiderata.

The test has been evolved from a consideration of Mitchell's ferrous tartrate test (ANALYST, 48, 1923, 1). This test was devised for quantitative work, and Mitchell, of course, makes no claim that it is specific for tannins, seeing that he uses it also for estimating gallic acid. Further, the test, as it stands, gives colourreactions with a number of phenolic substances, more especially if tap-water is used. It seemed, however, to the present writer that this test indicated possibilities worth investigating. Its use, of course, depends largely upon the well-known fact that iron is not precipitated from solution by commonly used reagents in the presence of tartrates. Mitchell used Rochelle salt and ferrous sulphate, and found that, with this reagent, tannin would not precipitate the iron, but that a bluish-violet coloration was obtained the intensity of which was related to the amount of gallic acid or gallotannin present.

It occurred to the writer that the test might possibly be so modified as to precipitate all tannins and no other water-soluble substances found in plant extractives. He did not quite succeed in obtaining this result with Mitchell's reagent, but by experimenting with ferric salts and citrates, he ultimately found that by using the iron and ammonium citrate of the British Pharmacopœia, together with ammonium acetate, an almost ideal reagent was obtained. A full list of results is given below, but for the moment it may be said that, with the exception of hæmatoxylin, the writer has so far been unable to find any other chromogenic water-soluble phenols which are precipitated by the method here described for the precipitation of tannins. Hæmatoxylin is readily distinguished, because it is only partially precipitated and yields a deep blue filtrate. Certain distinctive results were also obtained with several other phenolic substances, and will be described. By means of this test gallotannins can be readily and quickly distinguished and separated from gallic acid, and catechu tannins from catechins. Catechol tannins also can be quickly distinguished from such bodies as irongreening anthoxanthins, caffeo-tannic acid (so-called) and ipecacuanhic acid.

METHOD OF TESTING.—A solution of 0.25 grm. of iron and ammonium citrate in 100 c.c. of tap water is prepared. The iron compound (?) is often slightly acid, and if this is not rectified by the alkalinity of the tap-water, the solution should be made *very* slightly alkaline by the cautious addition of aqueous ammonia. It is important that the iron citrate should answer the pharmacopœial requirements as to general characters and purity, more especially as there is a green citrate, also sometimes used in medicine, which on no account must be used for this test. The actual method of applying the test depends upon the nature of the extractive and the purpose of the test. Preliminary experiments seem to indicate that the test may be advantageously used in certain cases as a quantitative method. The present paper, however, deals only with the qualitative use, in which two principal cases arise:

(1) If a freshly made, clear, aqueous extractive or solution has to be tested, place 4 c.c. of this in a test-tube, and add, successively, 4 c.c. each of the iron solution and of a 30 per cent. solution of ammonium acetate. Shake well. Note the colour or appearance, and then boil. Filter. Complete reaction should be ensured by testing a portion of the filtrate with more of the ferric citrate solution and observing if there is any further change. Note colour of precipitate (if any) and of filtrate or solution. Boil the latter with a little 10 per cent. solution of ammonia and note whether there is any further change. The precipitate should be insoluble in solution of ammonia or dilute acetic acid, but is soluble in dilute hydrochloric acid.

(2) If testing a pharmaceutical or other ready-made extractive which appears to be an alcoholic or concentrated aqueous preparation, it is advisable to proceed as follows:—Dilute sufficiently with 10 per cent. solution of ammonium acetate. Warm. Filter. Wash precipitate with successive small quantities of boiling water to dissolve salted-out tannin, and collect the washings with previous filtrate. Add the iron reagent and proceed as before. By this method resin, fat, chlorophyll and other substances which are likely to interfere with the success of the test are sufficiently removed. Some of the less soluble phlobaphenes, in the case of phlobotannin drugs, are also lost, but this is not a disadvantage, as these are scarcely to be regarded as true tannins.

STATEMENT OF RESULTS.—A very large number of pure substances and vegetable bodies have been tested, and some of the results may be summarised thus:

(1) True tannins appear to be completely precipitated from all substances known to contain them. With gallotannins a purplish precipitation commences in the cold and is complete on boiling. Without the ammonium acetate there is neither precipitation nor purple coloration. Indeed, if the iron reagent is boiled with the tannin solution before adding the ammonium acetate, subsequent precipitation becomes difficult or incomplete.

(2) The only other substance which has yielded a precipitate under the conditions named for tannins is hæmatoxylin, and this can be readily distinguished from tannin by giving a deep blue solution and no purplish precipitate in the cold. Further, on boiling with excess of the reagent partial precipitation, only, takes place, a blue-black precipitate and a deep blue filtrate being yielded. Logwood in fresh decoction gives a similar result.

(3) Catechol, protocatechuic acid, catechins, pyrogallol, gallic acid and brazilin (in the form of decoction of sappan wood), all give purplish-violet solutions on boiling. On the addition of solution of ammonia the colour changes to an intense reddish tint. There is no precipitate in any case.

(4) Carbolic and salicylic acids, resorcinol, hydroquinone, phloroglucinol, and anthraquinone give no characteristic result until the solution of ammonia is added, when there is some intensification of the brown colour.

(5) Quercetin, rutin, aloin, and, as far as can be judged from extractives containing them, all other water-soluble anthoxanthin and oxymethyl-anthraquinone bodies give a brown coloration which is considerably intensified on adding solution of ammonia. This result is also yielded by *Nux vomica* (caffeo-tannic acid, so-called), by hops (so-called hop-tannin, etc.) and probably by the majority of plant extractives which do not contain tannin. A certain number of extractives containing anthoxanthins (? flavones), if sufficiently strong, yield a precipitate *after* the addition of ammonia and reboiling, notably those of *Reseda luteola*, *Digitalis* leaves and *Stramonium* leaves. *Viburnum prunifolium* and cotton root barks appear to give a similar result. Alcoholic extractives treated by the second method generally answer best. This test distinguishes a reliable pharmacopœial tincture of *digitalis* made with properly collected and dried leaves from many other chlorophyll-containing tinctures, *e.g.* those of belladonna and hyoscyamus.

(6) Anthocyanin extractives which contain no tannin and little or no anthoxanthin, e.g blue cornflower and poppy petals in decoction, give no very characteristic result.

#### THE QUALITATIVE SEPARATION OF PHLOBOTANNIN, GALLOTANNIN AND GALLIC ACID IN SOLUTION.

This may be readily effected by combining Stiasny's test, as modified and extended by the present writer (ANALYST, 1924, 442), with the test described above.

METHOD.—Boil 10 c.c. of aqueous solution or extractive (diluted with water if alcoholic) with excess of 10 per cent. hydrochloric acid and 40 per cent. formaldehyde (12 drops of each are usually ample) for one minute. Cool and filter. The precipitate will contain all the phlobotannin present. The short period of boiling does not result in any very appreciable quantity of other phenolic bodies being precipitated. Therefore, if, after washing successively with water, 90 per cent. alcohol and 10 per cent. solution of ammonia, there is a residue left which is very obvious with respect to colour and quantity, it almost certainly indicates phlobotannin. Confirm by testing with bromine water or by any other suitable test applied to the original solution or extractive.

The filtrate from the formaldehyde test may be divided into two parts, one of which should be tested as described in the paper cited above for iron-greening or iron-blueing phenolic bodies. If iron-blueing occurs, the second portion should be neutralised by the cautious addition of a weak solution of ammonia, and tested by boiling with the ammonium ferric citrate and ammonium acetate solutions as

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described in the present paper. A purple or violet precipitate is due to gallotannin. If gallic acid be present, the filtrate (or solution, if gallotannin be absent) will be purplish-violet. In the event of the gallic acid content being small, the reddish colour which may be obtained by adding solution of ammonia is often more intense than the previously existing violet colour.

SUMMARY AND CONCLUSIONS .- A new test for tannins and certain other chromogenic phenols is described, the reagent used being the iron and ammonium citrate of the British Pharmacopœia together with ammonium acetate. Very distinctive results are obtained with tannins and hæmatoxylin. These results differ from one another and from those yielded by any other water-soluble Tannin alone is completely precipitated substances known to the writer. by the method employed. Hæmatoxylin is incompletely precipitated. No other water-soluble phenols or phenolic glucosides appear to yield precipitates in neutral solution, but a purplish-violet coloration is given by catechol, protocatechuic acid, catechin, pyrogallol, gallic acid and brazilin. This colour is changed to an intense reddish colour on the addition of ammonia. Vegetable extractives containing phenolic bodies other than those mentioned give an intense brown colouration, more especially after the addition of ammonia. Caffeo-tannic acid, so-called and the reputed tannin of hops are not precipitated. All the plant extractives which yield a precipitate in this test, give a marked response to the goldbeater's skin test and also give positive results with the modified and extended Stiasny's test, described elsewhere by the present writer. The test appears, therefore, to be quite specific for tannins, and also yields valuable results with certain other phenolic substances. It is of especial value in pharmacognosy, and plant analysis generally, and may prove to be useful for quantitative purposes.

UNIVERSITY COLLEGE, EXETER.

## Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

#### PUBLIC HEALTH (DRIED MILK) REGULATIONS, 1923.

CALCULATION OF "EQUIVALENT PINTS."

THE "equivalent pints" of a quantity of dried milk are given by the following formulæ, similar to those previously published (ANALYST, 1923, 48, 596) for condensed milk.

W. is the total weight of dried milk in grms., and F., T.M.S., and S.N.F. are the percentages by weight of fat, total milk solids and solids-not-fat, respectively, in the dried milk.

<i>Milk.</i> Equivalent pints = $\frac{F. \times W}{2107}$	or	$\frac{\text{T.M.S.}\times\text{W.}}{7258}.$
Three quarter cream milk. $F \times W$		ТМЅХW
Equivalent pints $=$ 1582	or	6797
Half cream milk.		
Equivalent pints = $\frac{F. \times W}{1056}$	or	$\frac{\mathrm{T.M.S.}\times\mathrm{W.}}{6335}.$
Quarter cream milk.		
Equivalent pints = $\frac{F. \times W.}{528}$	or	$\frac{\text{T.M.S.}\times\text{W.}}{5811}$
Skimmed milk.		
Equivalent pints = $\frac{S.N.F.}{528}$	$\frac{\times W}{5}$ .	

E. Hinks.

### CALCULATIONS: PUBLIC HEALTH (DRIED MILK) REGULATIONS, 1923.

UNDER the above Regulations it is necessary to calculate the number of pints of milk of stated composition which are equivalent to the contents of a tin of dried milk.

	Dried Milk.				
	Milk.	<sup>3</sup> ₄ Cream.	1/2 Cream.	‡ Cream.	
Composition of corresponding Fat standard milk T.S.	$3 \cdot 6$ $12 \cdot 4$	$2.7 \\ 11.6$	$1 \cdot 8$ $10 \cdot 8$	$\begin{array}{c} 0{\boldsymbol{\cdot}}9\\ 9{\boldsymbol{\cdot}}9\end{array}$	
Minimum limit of fat per cent	26.0	20.0	14.0	8.0	
Sp. Gr. of standard milk	1.032	1.0328	1.034	1.0347	
Formulæ, for calculation from T.S. found of equivalent milk in ounces	$\frac{\text{C.}\times\text{T.S.}}{362\cdot7}$	$\frac{C.\times T.S.}{339\cdot 6}$	$\frac{\text{C.}\times\text{T.S.}}{316\cdot6}$	$\frac{\text{C.}\times\text{T.S.}}{290\cdot4}$	
Formulæ, for calculation from fat found of equivalent milk in ounces	$\frac{\mathrm{C.}\times\mathrm{F.}}{105\cdot3}$	$\frac{\mathbf{C.}\times\mathbf{F.}}{\mathbf{79\cdot06}}$	C.×F. 52·76	$\frac{\mathbf{C.} \times \mathbf{F.}}{26.40}$	
Per cent. of fat when dry "dried milk" of minimum limit fat con- tent is diluted to contain the prescribed total solids	$3 \cdot 22$	2.32	1.51	0.79	

C = Weight of dried milk in tin in grms.

#### NOTES

It is evident from the above figures that it is impossible to dilute dry "dried milk" of minimum limit fat content to milk of standard composition.

The following table shows the composition of each variety of dried milk containing the minimum percentage of fat, which when diluted to the volume calculated from the T.S. would produce standard milk.

		Milk.	3 Milk.	12 Milk.	¼ Milk.
Water	••	10.44	14.08	16.00	12.00
Fat		26.00	20.00	14.00	8.00
S.N.F.		$63 \cdot 56$	65.92	70.00	80.00

Below are tabulated the percentages of fat corresponding to percentages of moisture in each variety of dried milk, which when diluted to the volume calculated from the total solids will yield the standard milk.

D.C. F.

	Per Cent. Fat.								
Per cent. Moisture.	Milk.	<sup>3</sup> / <sub>4</sub> Milk.	1 Milk.	<u></u> ∦ Milk.					
0	29.03	$23 \cdot 28$	16.67	9.09					
1	28.74	23.04	16.50	9.00					
2	28.45	$22 \cdot 81$	16.33	8.91					
3	28.16	$22 \cdot 58$	16.17	8.82					
4	27.87	22.35	16.00	8.73					
<b>5</b>	27.58	22.11	15.83	$8 \cdot 64$					
6	27.29	21.88	15.67	8.55					
7	27.00	21.65	15.50	8.45					
8	26.71	21.41	15.33	8.36					
9	26.42	21.18	15.17	8.27					
10.44	26.00	_							
12.00			<u> </u>	8.00					
14.08	_	20.00							
16.00	<u> </u>		14.00						

The table is used for calculation thus:

If the "dried milk" contains the same or more fat than the figure given in the table to correspond with the moisture found, the dilution is calculated from the total solids and will give a milk of standard composition as regards total solids with a fat equivalent to or more than the standard. If the milk contains less than the fat corresponding to moisture found, the dilution is calculated from the fat, and the resulting milk will contain the standard amount of fat with an excess of total solids.

DOUGLAS HENVILLE.

#### ERRATUM.

#### CONDENSED MILK REGULATIONS, 1923.

ANALYST, 1923, 48, 597, line 13 from bottom: For "total milk solids in the tin" read "total milk solids in one pint."



## NEW FLASK FOR USE WITH SOXHLET'S APPARATUS.

THE flask employed with the Soxhlet apparatus is commonly unnecessarily large and heavy. The flask illustrated has been made for the writer and found very satisfactory in practice. It is made of thin glass and is very light in weight. In addition to giving increased accuracy, the distillation is accomplished with the minimum of heat and the extract is dried with greater rapidity.

ROBERT C. FREDERICK.

ROYAL NAVAL MEDICAL SCHOOL, ROYAL NAVAL COLLEGE, GREENWICH.

## Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

#### CITY AND COUNTY OF KINGSTON-UPON-HULL.

REPORT OF THE PUBLIC ANALYST AND BACTERIOLOGIST FOR 1923.

DURING the year 1068 samples of foods and drugs were examined, of which 538 were purchased informally. Of the total number, 58 were reported as adulterated and 33 as suspicious, the percentage of the two being 8.5, as compared with 12.0 in 1922. The number of samples per 100,000 of the population was 372, as compared with 300 for England and Wales during 1921.

MILK.—Of the 436 samples examined, 23 were adulterated and 23 suspicious. Eleven samples contained an unwarranted amount of "dirty" sediment, and 6 were returned as adulterated for this reason. Proceedings were taken against a farmer who had supplied 3 of these "dirty" milks. These samples were proved in court to be seriously contaminated with dung, and the Corporation won an appeal in the High Court on the method of sampling adopted, but the local magistrates finally dismissed the summons on the ground that there was no legal standard for the proportion of extraneous sediment in milk.

DRIPPING.—Two samples (from the same shop), out of 13 examined, were adulterated. They contained about 14 per cent. of water, 1 per cent. of salt, and **3.6** per cent. of non-fatty organic impurities (flour, etc.). Proceedings were taken in the case of one of these samples, and evidence was given that dripping should not contain more than small amounts (up to 2 per cent.) of water and other extraneous matters; this definition was in agreement with the Ministry of Health standard for dripping during the war. The justices, however, decided that the substance sold was "dripping," and dismissed the case. FLOUR AND BREAD.—Of a total of 10 samples of flour, 4 contained potassium persulphate, a so-called "improver," and 3 of the 4 were also slightly bleached with nitrogen peroxide. In the present state of the law this treatment of flour cannot be stopped.

FARINACEOUS FOODS.—Four samples of pearl barley and 3 of arrowroot were adulterated. The pearl barley contained about 1 per cent. of rice flour as a "facing" over the grains of barley. The adulterated arrowroot samples consisted of cream of tartar (1) and maize flour (cornflour) (2). They were probably all accidental substitutions.

CANNED FOODS.—Three of 6 samples of canned tomatoes contained  $5\cdot 2$ ,  $3\cdot 1$  and  $1\cdot 9$  grains of tin, respectively. All came from one vendor, who was convicted.

DRUGS.—Of 158 samples examined, 9 were reported to be adulterated. These were:—Almond oil (2), which consisted largely of a foreign kernel oil; milk of sulphur (2), containing about 37 per cent. of hydrated calcium sulphate; milk of sulphur (1), containing 25 parts of arsenious oxide per million; sweet spirit of nitre (2), deficient to the extent of 40 and 42.8 per cent. in ethyl nitrite; tincture of quinine (1), deficient 10 per cent. in alcohol; and turpentine oil, which consisted wholly of a petroleum distillate.

BACTERIOLOGICAL EXAMINATIONS.—In all, 3,744 specimens were examined, 3,733 of which were pathological material, and 11 were samples of water.

A. R. TANKARD.

#### CITY OF BIRMINGHAM.

#### ANNUAL REPORT OF THE CITY ANALYST FOR 1923.

OF the 5,197 samples analysed during the year, 4,518 were taken under the Sale of Food and Drugs Acts, and of these, 3,939 samples were bought informally. With the exception of milk, samples were rarely bought formally unless a previous informal sample had been found to be adulterated. The number of samples purchased was at the rate of 483 for every 100,000 persons living in the city.

MILK.—During the year 2,441 samples of milk were analysed, being at the rate of 261 per 100,000 persons, and, of these, 158 were adulterated.

CONDENSED MILK.—The Regulations appear to be defective in making no distinction between the composition of condensed skimmed milk and condensed machine-skimmed milk. One of the samples received was marked "skimmed" on the declaration, and "machine-skimmed" on another part of the label. As it only contained 0.4 per cent. of milk fat, the declaration was incorrect, as *uncondensed* skimmed milk may contain 1 per cent. of fat. The vendor of the sample was cautioned. Five other samples examined practically complied with the Regulations.

BUTTER.—Seventy-six per cent. of the samples were free from boric acid, and in the remainder the quantity did not exceed 0.5 per cent.

GOLDEN SYRUP.—Only 3 of 9 samples were genuine, the others containing from 25 to 90 per cent. of glucose syrup. A circular was sent to members of the grocery trade calling attention to the necessity of mixtures of golden syrup and glucose syrup being suitably labelled and not sold as "golden syrup."

DRUGS.-Twenty-six of the 218 samples examined were unsatisfactory.

Camphorated Oil.—Four samples were practically correct (19.7 to 20.2 per cent. of camphor), but two from one vendor contained 13.7 per cent. and 14.9 per cent., and the vendor was prosecuted and fined.

*Boric Acid Powder.*—Nine samples contained from 4 to 24 parts of lead per million, and one sample contained 80 parts, for the sale of which the vendor was cautioned.

Potassium Carbonate.—Two samples from one vendor contained about 80 parts of lead, and 7 and 10 parts of arsenic per million, with 20 per cent. and 17.9 per cent. of moisture, respectively. The vendor was prosecuted and it was proved that when the drug was sent to the shop it complied with the Pharma-copoeial requirements, and the explanation given was that the drug had dissolved lead and arsenic from the shop bottle. The magistrates dismissed the case on the ground that the drug was "unavoidably mixed with some extraneous matter in the process of collection or preparation," and that "collection" included storage (cf. ANALYST, 1923, 48, 215, 260). Experiments made subsequently proved that the explanation was correct (cf. ANALYST, 1923, 48, 543).

J. F. LIVERSEEGE

## Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

#### SALE OF "BUTTER MIXTURE."

ON August 13th a dairyman was summoned at Salford for selling an article not of the nature, substance and quality demanded, and an Irish firm of margarine manufacturers was summoned for aiding and abetting.

Mr. R. H. Wright, for the prosecution, said that the inspector sent a messenger for half a pound of "butter mixture"—not margarine. The analysis showed the sample to contain only 1 part of butter in 200, so that, whatever "butter mixture" might mean, this sample could not be said to be butter mixture. The article was supplied by the defendant company and was accompanied by advertisement slips referring to it as "butter mixture."

Mr. Sandbach, for the defence, submitted that, in view of rulings, the firm had a right to describe the article as "butter mixture" if they wished; but, as the Stipendary had recently given a decision on the point, they did not intend to exercise that right, and had withdrawn altogether the description "butter mixture," so as to fall into line with the Stipendiary's view of the law. According to a decision in the King's Bench Division his clients had a right to describe a mixture of margarine and butter—no matter what the proportions were—as "butter mixture," but they had no wish to do so.

The Stipendiary said that as the offence was practically admitted, the defendant would be fined 20s. and the manufacturers 40s.

A second summons for selling the sample in a wrapper having on it a descriptive name other than the word "margarine," was dismissed, as the Stipendiary considered that the use of the fancy name was covered by the decision in *Hawes* v. *Stephens*, but fines were imposed for the use of a wrapper bearing the word "margarine" otherwise than in  $\frac{1}{2}$  inch block letters.

## Tests on Volumetric Glassware. Classes A & B.

## THE NATIONAL PHYSICAL LABORATORY, TEDDINGTON, MIDDLESEX. METROLOGY DEPARTMENT. SEPT. 1924.\*

INSTRUCTIONS as to transmission, insurance and custody of apparatus, are followed by regulations governing the two classes of tests.

#### UNITS OF VOLUME.

(1) The Litre.

The litre is defined as the volume occupied by one kilogramme of water at its temperature of maximum density and subjected to normal atmospheric pressure.

(2) The Cubic Centimetre.<sup>+</sup>

This is the volume occupied by a cube each of whose edges is one centimetre in length.

The accepted relation between the cubic centimetre and the millilitre is  $1000 \text{ ml.} = 1000 \cdot 027 \text{ c.c.}$ 

#### (3) British Imperial Units.

The gallon is defined as the volume occupied by ten imperial pounds weight of distilled water as weighed in air against brass weights, with both the water and the air at a temperature of  $62^{\circ}$  F. and the barometer at 30 inches.

> The gallon has now been legalised as 4.5459631 litres. The cubic inch is equivalent to 16.38659 ml.

(4) The G.W.A. Unit.

This is defined by the relation 1000 G.W.A. = 1002 ml.

#### Marks.

Flasks.

NP.A. NP.B.

24 24 24 respectively denote that the apparatus is correct within the specified tolerance and certificates are issued for Class A where required.

#### TOLERANCES.

	Capacity ml		10	25	50	100	250	500	1000	2000
Α	Tolerance $\pm$ ml. for con	ntent	0.012	0.03	0.04	0.06	0.1	0.15	0.2	0.4
в	Tolerance $\pm$ ml. for co	ntent	0.02	0.04	0.06	0.1	0.2	0.3	0.4	0.6
	for delivery				<u> </u>	$0 \cdot 2$	0.4	0.6	0.8	1.0

Note.—(a) For capacities not tabulated, the tolerance is that of the next larger tabulated capacity.

#### Pipettes.

	Capacity ml.	••	• •	<b>2</b>	<b>5</b>	10	<b>20</b>	30	50	100	250
Α	Tolerance $\pm$ ml. for	or cont	ent	0.01	****		0.02	0.03	0.04	0.06	0.10
В	delivery	••		0.02	0.03	0.04	0.05	0.06	0.08	0.12	$0 \cdot 2$

\* The Director of the National Physical Laboratory, Teddington, Middlesex, has kindly offered to supply members of this Society with a copy of this pamphlet, free of charge, on application being made to him.—EDITOR.

 $\ensuremath{+}$  The use of the millilitre to express the capacity of volumetric glassware is strongly recommended.

#### TESTS ON VOLUMETRIC GLASSWARE

Gra	iduated Pipettes.								
	Total capacity ml		•••	2	5	10	30	50	100
Α	Maximum error allowed at a and also maximum different tween the errors at any two for content or delivery $\pm m$	ny poin nce allo 70 point 11.	t tested wed be- s tested	0.01	0.02	0.03	0.06	0.1	0.15
В	Maximum error allowed at a and also maximum differe tween the errors at any tw $\pm$ ml.	ny poin nce allo 70 point	t tested wed be- s tested	0.02	0.04	0.06	0.1	0.2	0.3
	See	Notes (	a) and $(b)$	under	Burettes.				
Bu	rettes.								
	Total capacity ml	••	2	5	10	30	50	100	200
A	Maximum error allowed a point tested and also max difference allowed betwee errors at any two points	t any imum n the tested	0.01		0.00	0.00	0.00		0.0
ъ	for content or delivery $\pm$ m	u	0.01		0.02	0.03	0.00	0.1	0.5
в	Maximum error allowed a point tested and also max difference allowed betwee errors at any two points	t any imum n the tested		. •					
	$\pm$ ml	••	0.02	0.03	0.04	0.06	0.01	0.02	0.4
	Note.—(a) For capacities no	ot tabula	ated, the	tolerand	ces are th	ne same	as thos	e given	for the
	(b) The tolerances a of it. Thus for example $\pm 0.1$ ml. (Class B) at an two points tested does	pacity. pply to e, a 50 ny point not exce	the whol ml. buret providec eed 0.06	e of the te may i that ti ml. (Cla	graduate be in err he differe ss A) or	ed porti or by <u>-</u> nce bet 0·1 mi.	on and $\pm 0.06$ m ween th (Class 1)	to any f nl. (Clas le errors B).	raction s A) or at any
Gra	duated Cylinders.	_			,			,	2000
	Total capacity ml	5	10 23	5 50	100	250	500	1000	2000
A	Maximum error allowed at any point tested, and also maximum difference al- lowed between the errors at any two points tested:								
	for content $\pm$ ml	0.04	0.06 0	·1 0·2	2 0.4	0.6	1	<b>2</b>	3
В	›› <b>›</b> ›	0.06	0.1 0	$\cdot 2  0 \cdot 4$	<b>4</b> 0·8	1.5	<b>2</b>	4	8
	Note.—The notes (a) and (b) cylinders.	relating	to tolera	nces on l	burettes (	supra) a	apply al	so to gra	duated
Spi	ecific Gravity Bottles or Tu	bes.							
	Capacity ml 10	25	50	<b>75</b>	100	15	0 2	200	250
Α	Tolerance $\pm$ ml 0.003	0.002	0.008	0.01	0 0.01	2 0.0	015 0	0.020	0.025
Ga	$s$ Analysis Vessels. $\begin{cases} m_{pi} \\ m_{M} \end{cases}$	easuring pettes. easuring tubes	bulbs. tubes, g , etc.	as buret	tes, eudio	ometers	, nitron	neters, 1	oressure
	Graduated	l measu	ring app	aratus 1	ot sub-d	livided.			
	Capacity ml.		. 10	<b>25</b>	50	10	0 2	250	
	A Tolerance $\pm$ ml.		. 0.015	0.03	0.04	0.	06 (	)•16	
	B Tolerance $\pm$ ml.	•	. 0.03	0.06	0.08	3 O·	12 (	0.20	
2	Detailed regulations as	to con	structio	on of v	essels o	f each	type	are giv	en for

both classes, and it may be noted that vessels intended for delivery (excepting

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pipettes) are not accepted for Class A; cylinders are not accepted for delivery for either Class A or B; and only flasks of over 100 ml. capacity for B.

Apparatus not specifically dealt with in the pamphlet may be submitted for testing and is subject to special terms.

Vessels graduated in "G.W.A." units, that is Mohrs grammes or cubic centimetres (1000 G.W.A. =1002 ml.) are accepted for either class A or Class B tests, and the tolerances given above for vessels graduated in millilitres apply, and a special mark  $\mathbf{X}A$  or  $\mathbf{X}B$  is used. 24. 24.

The pamphlet concludes with a list of verification and other charges.

D. G. H.

# Joint Committee for the Standardisation of Scientific Glassware.

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#### REPORT No. I. ON UNITS OF VOLUME.

THE Joint Committee for the Standardisation of Scientific Glassware, working under the aegis of the Institute of Chemistry, and having members representing the users, manufacturers, dealers, and Government Departments interested in scientific glassware, has issued the subjoined report:\*

#### REPORT ON UNITS OF VOLUME.

The Committee have given much careful consideration to the question of units of volume, and as a result of their deliberations they unanimously recommend:

That the recognised international metric units—the "litre" (l) and "millilitre" or thousandth part of the litre (ml)—shall be used as the standard units of volume, and that standard volumetric glassware shall be graduated in terms of these units and marked "ml" instead of "c.c."

In making this recommendation, the Committee have had in mind the great advantages to be gained by the general use of a uniform system which has been recommended by many scientific bodies, and is at present already extensively used, notably in America. The substitution of the millilitre for the cubic centimetre involves no practical difficulties as the two units differ only very slightly in magnitude. The difference in capacity between a 1000 c.c. and a 1000 ml. flask is, for example, only one seventh of the permissible error on a standard 1000 ml. flask.

In the course of the discussions, however, it became evident that some chemists still prefer to use Mohr's system of units, and would be unwilling at present to change their existing practice. It was clear, therefore, that some temporary inconvenience would be caused by an immediate complete withdrawal of official recognition of Mohr's units.

\* Copies of this Report may be obtained from the Secretary of the Committee, Institute of Chemistry, price 6d., post free.

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In face of these facts the Committee have felt it desirable to couple with the above recommendation certain proposals designed to remove the confusion at present existing between the two systems of units. These are:

(1) That the unit of volume on Mohr's system shall in future be designated "G.W.A.,"\* and that these letters shall be marked on all volumetric glass vessels graduated on the basis of Mohr's system, and shall be used by chemists when reporting results obtained by the use of such vessels.

#### (2) That the "G.W.A." unit shall be defined thus:

#### 1000 G.W.A. = 1002 ml.

These additional recommendations will enable the two systems to be used side by side with a minimum of inconvenience during the transitional period which the Committee realise must precede the universal adoption of the litre and millilitre for general chemical work.

The Committee understand that in view of the above recommendations the National Physical Laboratory will accept for test<sup> $\dagger$ </sup> vessels graduated on the basis of G.W.A. units, and clearly marked to indicate this, and will place a distinctive mark on approved vessels graduated on this system, but not the Laboratory monogram **NP**, which will be reserved for vessels graduated in millilitres.

Information relating to the two systems of units, and the reasons underlying the above recommendations are given in the following notes.

#### METRIC UNITS OF VOLUME.

The volume of a body of simple geometrical shape can readily be calculated from the linear dimensions of the body. Hence, once the unit of length has been decided upon, the unit of volume should theoretically be defined in terms of the unit of length. The volume of a cube each of whose sides is of unit length becomes automatically the unit of volume; such a definition by its logical simplicity makes an instant appeal to the mind, and it is therefore natural to find in common use such units as the cubic centimetre and the cubic foot, based on the corresponding units of length.

Volumetric measurements, however, are most extensively used when dealing with fluids, and hollow vessels of known capacity have long been used for measuring volumes of liquid. But while it is extremely difficult to determine accurately the capacity of a hollow vessel from measurements of its internal dimensions, to determine the weight of liquid required to fill a vessel is, on the contrary, an operation which may be carried out easily and to a high degree of precision. Hence, units of volume have come into use which are not defined in terms of the units of length, but as the volumes occupied by specified weights of a particular liquid—usually water. The gallon and the litre are units of this kind.

Two distinct types of units of volume have thus come into general use. Sooner or later under any system the necessity arises of determining the relation between the two types of units, of determining for example, the number of gallons in a cubic foot. In the older systems of units the two types of units of volume were defined independently of each other, and as a result no simple numerical relation exists between them. The number of gallons in a cubic foot, for example, is not represented by a simple whole number.

One of the objects of the founders of the Metric System was to secure a simple numerical relation between the two types of units of volume. It was intended to achieve this by defining the unit of mass, the kilogramme, as the mass of a quantity of water which at its temperature of maximum density occupied a cubic decimetre. The unit of volume, the litre, could then be defined indifferently either as a cubic decimetre or as the space occupied by a kilogram of water at its temperature of maximum density.

A cubic decimetre of water is, however, manifestly unsuitable for practical use as a standard weight. To give practical effect to the system it was necessary to make a standard kilogramme weight whose mass should be in accordance with the definition laid down. A standard kilogramme weight—the "Kilogramme des Archives"—was prepared with great care and skill at

#### \* Vide infra.

<sup>†</sup> A pamphlet giving details of the tests on volumetric glassware carried out at the National Physical Laboratory may be obtained free of charge on application to The Director, The National Physical Laboratory, Teddington, Middlesex.

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the end of the eighteenth century, but during the nineteenth century distrust in the accuracy of the work arose. Consequently in 1872 the *Commision Internationale du Metre* discussed the matter fully in all its bearings and decided that the International Kilogramme should be deduced from the Kilogramme des Archives in its actual state. The original definition of the kilogramme was thus abandoned, and the kilogramme was re-defined as the mass of a particular standard weight.

The definition of the litre was subsequently revised\* in conformity with this change, and the accepted definition at the present time is:—

"The unit volume for determinations of high precision is the volume occupied by a mass of one kilogramme of pure water at its temperature of maximum density and under normal atmospheric pressure<sup>†</sup>; this volume is termed the litre."

It is important to observe that the definition of the litre is now absolutely independent of the metric units of length. The cubic centimetre, on the other hand, being simply the volume of a cube whose edges are one centimetre long, is completely defined without any reference to the volume of a mass of water. Thus no direct relation between the litre and the cubic centimetre results from the definitions of these units. This relation can only be obtained by direct experimental determination, and the most accurate determination available is that carried out at the Bureau International des Poids et Mesures. M. Benoit<sup>‡</sup> in his summary of the work gives as the most probable value

#### 1 litre = $1000 \cdot 027$ c.c.

and states that the uncertainty of this value probably does not exceed one unit in the last decimal place.

The difference between the cubic centimetre and the millilitre is so small as to be negligible for ordinary volumetric glassware; the difference in capacity between a 1000 c.c. flask and a litre flask, for example, is less than the observational errors liable to arise in the ordinary use of either flask.

The term "cubic centimetre" has, however, been misapplied by the users of Mohr's system (see below) to denote the volume of a quantity of water having an apparent weight in air of 1 gramme. A flask which contains an amount of water weighing 1000 grammes in air has a capacity of almost exactly 1002 c.c. To speak of such a flask as a 1000 c.c. flask is clearly inadmissible. Volumetric glassware, manufactured by the leading British firms, and marked "c.c.," may safely be relied upon as having been calibrated on the basis of the cubic centimetre. Volumetric glassware of foreign manufacture similarly marked "c.c.," may have been calibrated in terms of either the cubic centimetre or grammes of water.

In view of this confusion in the use of the term cubic centimetre, and of the fact the cubic centimetre is not exactly one thousandth part of a litre and further, because the mass of water which occupies I c.c. under definitely specified conditions cannot be directly derived from the accepted definition of the litre, the Committee adopted the recommendation given above, *viz*.:--

That the recognised international metric units—the *litre* (l) and *millilitre* or thousandth part of the litre (ml)—shall be used as the standard units of volume, and that standard volumetric glassware shall be graduated in terms of these units and marked *ml*. instead of *c.c.* 

The acceptance of this recommendation by chemists and manufacturers of volumetric glassware would bring the practice in this country into line with that in other countries, notably America, and would give effect to the recommendation of numerous scientific bodies that the litre, as defined above, should be exclusively used as the unit of volume in all scientific work. The publication of all results in terms of millilitres would secure a uniformity which is at present lacking, and remove the uncertainty due to the term cubic centimetre being used sometimes correctly, sometimes as equivalent to the millilitre, and sometimes as the space occupied, under conditions not generally well defined, by a quantity of water which has an apparent weight in air of one gramme.

#### MOHR'S SYSTEM.

According to Mohr's original proposal a "litre" flask would be adjusted so that when filled with water at  $17.5^{\circ}$  C. it would contain an amount of water which, when weighed in air against brass weights, had an apparent weight of 1000 grammes. Such a flask would contain almost exactly 1002 c.c. The term cubic centimetre was misapplied to the thousandth part of this volume. This misuse of both the terms litre and cubic centimetre still persists.

#### \* Trav. et Mem., Vol. 12, 1920.

<sup>†</sup> The reference to normal atmospheric pressure perhaps requires a word of explanation. Water is slightly compressible, and hence the volume of any given quantity of water varies slightly with the pressure to which it is subjected. Hence, to be precise, the definition of the litre must state the pressure to which the water is to be subjected.

<sup>‡</sup> Trav. et Mem., Vol. 14, 1910.

Some chemists still maintain that it is more convenient in practice to use as a unit of volume the space occupied by a quantity of water which has an apparent weight of 1 gramme in air at ordinary room temperature.

To avoid confusion resulting from the use of the terms 'litre' and 'cubic centimetre' in connection with such units, the Committee recommend (see (1), page 2) that the letters "G.W.A." —a mnemonical abbreviation for 'grammes of water in air"—shall be used in describing such units.

It is further necessary that an exact definition of the "G.W.A." unit be adopted.

A quantity of water which weighs 1000 grammes in air of density 0.0012 grms./ml. when weighed against brass weights of density 8.4 grms./ml. occupies a volume of 1002.021 ml. at  $60^{\circ}$  F. This volume differs from 1002 ml. by only two parts in a hundred thousand, which is negligibly small in comparison with the tolerances allowed on volumetric glassware, and the accuracy attainable in the ordinary use of such glassware. Hence the committee on grounds both of convenience and precision have adopted the definition given in recommendation (2), above, namely:

$$1000 \text{ G.W.A.} = 1002 \text{ ml.}$$

This relation defines the G.W.A. unit in a simple and accurate manner, and at the same time gives it a value which differs only by a negligible amount from the volume occupied at room temperature ( $60^{\circ}$  F.) by a quantity of water which has an apparent weight of 1 gramme when weighed in air against brass weights.

The above definition enables conversion from millilitres to G.W.A. units and vice versa to be easily made, and will enable the two units to be used side by side without confusion during the transitional period which must elapse before the universal adoption of the litre and millilitre is obtained in this country.

August, 1924.

## Carbon Monoxide in Public Gas Supplies

REPORT TO THE BOARD OF TRADE.\*

FROM 1812, when a public gas supply was started in London, until about 1840, the gas was produced by the carbonisation of coal in iron retorts, and contained from 3 to 8 per cent. of carbon monoxide. By about 1860 fireclay retorts had been generally adopted, and the proportion of carbon monoxide consequently increased by about 1 to 2 per cent. The average proportion throughout the country from about 1860 to the early nineties may be taken to have been 7 to 8 per cent., and nearly 30 per cent. of the gas still sold in England and Wales is such coal gas without admixture. If a gas undertaking makes only ordinary coal gas it has to find a market for a relatively large quantity of coke (75 to 80 lbs. for each 1000 cb. feet of gas it sells). Hence, if the coke does not return a fair proportion of the cost of the coal, more must be added to the price of the gas. The alternative is to use some of the coke for gas-making, and the gas made from coke, by any process practically available, is of the general character of water-gas and contains considerably more carbon monoxide than ordinary coal gas.

In 1921 the quantity of water-gas made by authorised gas undertakings in England and Wales was 48,130 million cb. feet, in the production of which 1,207,000 tons of coke and 51,573,577 gallons of oil were used. To obtain coal gas equivalent in heating power to this water gas about 3 million tons of coal would have had to be added to the 14,168,094 tons carbonised in 1921, and a market would have had to be found for an additional 2,700,000 tons of coke.

Computation of the Proportion of Carbon Monoxide in Gas. Adopting the average amount of 8 per cent. for the carbon monoxide in coal gas, and 42 per

\* By W. J. A. Butterfield (one of the Gas Referees). With correspondence arising thereon. H.M. Stationery Office. 1924. 2s. 6d. net.

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cent. for the carbon monoxide, in uncarburetted or blue water gas (which percentage, when the gas is carburetted, is diminished by about 4 for every gallon of oil used per 1000 cb. feet of the carburetted gas), it is possible to calculate the average proportion of carbon monoxide in the gas made by any undertaking over a given period, by the use of the formula—

$$\frac{8C + (42 - 4X)W}{100}$$

in which C is the percentage of coal gas, W the percentage of water gas (blue or carburetted), and X the number of gallons of oil used per 1000 cb. feet of carburetted water gas made. Since the mixed gas consists only of coal gas and water-gas (blue or carburetted), W = (100 - C).

This formula gives results sufficiently accurate for all necessary deductions as to the toxicity of public gas supplies in England and Wales at different times. It is not, without modification, applicable to Scotch supplies, because the coal gas, as produced from most Scotch coals, contains more than 8 per cent. of carbon monoxide.

Spasmodic analyses of the gas supplied in any area give little information as to the average proportion of carbon monoxide over a period of, say, 12 months. All that is needed for the application of the formula, however, is that gas undertakings should be under obligation to supply to the Board of Trade certified statements of the quantities of coal gas and water-gas made, and of coal and oil used in the manufacture, during the period of enquiry. Any gas obtained per ton of coal, in excess of 12,700 cb. feet, may be regarded as water gas in so far as its content of carbon monoxide is concerned, without risk of any serious error being incurred. This formula has been utilised for an exhaustive investigation into the proportions of carbon monoxide in the gas supplied by practically every gas undertaking in England and Wales during the past ten years.

Fatalities from Gas Poisoning.—Definite information has also been obtained as to the number of gas poisoning fatalities from the Registrar-General's Department. From a consideration of the various factors involved the following conclusions (inter alia) have been drawn:-The death rate from accidental gaspoisoning in the last 10 years is approximately one per annum per 350,000 to 400,000 persons. It is much lower in the small towns and villages, and this difference appears to be determined, not by the proportion of carbon monoxide, but by differences in housing conditions, uses to which the gas is put, and condition of gas pipes and fittings. Prior to the last five or six years the steady increase in the proportion of carbon monoxide in the gas was not attended by any increase in the death rate from gas poisoning, whilst the slight increase in the death rate during the last five or six years (during which there has been an increase in the proportion of carbon monoxide in the gas supplied) coincides with the advent of a period of neglect of internal gas piping, fittings, etc., in the case of supplies through ordinary meters. On the other hand, an extremely low death rate is associated, with prepayment meters, for the pipes and fittings of which the gas undertakings are usually responsible.

RECOMMENDATIONS.—The following recommendations are made, as following from the conclusions drawn in this Report:

I. That the inquiries instituted as from January, 1922, by the Board of Trade, in collaboration with the Ministry of Health, into the circumstances of every fatality from poisoning by gas from public supplies, be continued; the information afforded thereby be incorporated in periodical reports, and be utilised

as a guide in formulating measures for reducing the risks of gas poisoning. The reports might suitably cover periods of three or five years.

II. That the gas industry be asked to submit to the Board of Trade at an early date suggestions for a system of periodical inspection, and of maintenance in safe condition, of gas piping, fittings and appliances in dwelling houses.

III. That the suggestions received accordingly, subject to such additions or modifications as the Board of Trade may think necessary, be the basis of a scheme of inspection and maintenance of gas piping, fittings and appliances, which all gas undertakings specified by the Board of Trade shall be required to adopt and carry into effect without delay.

IV. That the gas industry be asked, after conferring with the makers of gas fittings and appliances, to submit to the Board of Trade proposals for the elimination from the trade of (1) types and qualities of fittings, etc., which are liable, after a few years' use, to become unsound or otherwise unsafe; and (2) flueless "heaters" or other appliances which are apt to evolve carbon monoxide. Also to submit proposals for preventing geysers, etc., being fitted in very small rooms without adequate and trustworthy vents to the open air for the products of combustion.

V. That these proposals, subject to such additions or modifications as the Board of Trade may think necessary, be recommended for adoption forthwith by all gas undertakings, and by all makers, dealers in and vendors of gas fittings and appliances in this country. That if such recommendation fails to prevent, within one year or at most two years, the supply to gas consumers of untrustworthy or unsafe gas fittings and appliances, the Board of Trade shall take steps (in regard to which it may ask, if necessary, the assistance of an advisory Committee) to secure to Local Authorities powers to stop the sale and supply in their districts of gas fittings and appliances which do not fulfil such requirements as to trustworthiness and safety as may be laid down from time to time in such manner as it may direct.

## Ministry of Agriculture and Fisheries.

#### INVESTIGATIONS INTO THE CAUSES OF THE UNUSUAL MORTALITY IN ENGLISH OYSTER BEDS IN 1920 AND 1921.\*

THE possible causes investigated include (1) direct poisoning, (2) disease due to parasites, (3) weakening of the oysters due to the abnormal summer, with subsequent natural death, (4) unusual attack by marine organisms. No definite cause has been traced; no single organism has been found common to all the dying oysters, nor any single symptom, neither has any evidence been found indicating that death might be due to T.N.T. poisoning resulting from the dumping of explosives, although it is possible that the enquiry was started at too late a stage for the detection of this.

The following test has been devised to detect 1 part of T.N.T. in 50 millions when two litres are available. The water is acidified with 25 c.c. of 10 per cent. sulphuric acid and extracted with 50 c.c. of benzene; after separation the benzene is evaporated to 5 c.c., 20 c.c. of alcohol are added and then 2 c.c. of 10 per cent.

\* Part II. Chemical Reports, etc. (Ministry of Agriculture and Fisheries, Ser. II., Vol. 6, No. 4, 1924). Pp. 69. H.M. Stationery Office. Price 7s. 6d. net.

sodium hydroxide solution, when the development of a fugitive red or pink colour indicates the presence of T.N.T. The colour so obtained gradually changes to brown, and is available after half an hour for quantitative estimation by matching against standard solutions of T.N.T. similarly treated.

Bacteriological tests on healthy specimens indicated total organisms growing on agar at 20° C. from 250 to 8000, and generally the presence of *B. coli* in fair numbers; cladothrix and streptococci are usually absent. Arsenic is present in oysters, especially in those from certain beds, those from Whitstable containing in some cases as much as 3.7 parts per million, and a few contain copper and zinc. Numerous detailed chemical and bacteriological analyses are given. The following is a typical analysis of oyster meat: Water, 78.7; fat, 1.9; proteins, 11.2; carbohydrates, 6.0; ash, 2.2; glycogen, 4.4 per cent.

H. E. C.

### ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

## Food and Drugs Analysis.

Estimation of Maltose in Presence of other Reducing Sugars by means of Barfoed's Solution. P. Nottin. (Comptes rend., 1924, 179, 410-413.)-Contrary to Le Grand's statement that maltose does not reduce Barfoed's solution under conditions specified (ANALYST, 1921, 46, 406), the author finds that the reduction effected by maltose in less than 1 per cent. solution is equal to that caused by 7 per cent. of its weight of dextrose, and diminishes as the concentration of the maltose increases. On the average the reduction of Bertrand's solution by maltose is equal to that of 57.2 per cent. of its weight of dextrose; this ratio varies with the concentration of the maltose, but may be calculated from Bertrand's tables. Thus the proportions of maltose and dextrose present in a solution containing about 0.5 per cent. of reducing sugars, expressed as dextrose, may be calculated as follows: -If A and T are the reducing powers of the solution determined according to the exact methods given by Le Grand and Bertrand respectively, and G and M the amounts of dextrose and maltose, A = G + 0.07M and T = G + 0.572M, from which M = 1.995(T-A) and G = A - 0.07M. Application of this procedure to various mixtures of dextrose, maltose and dextrin has given results in accord with polarimetric measurements. Т. Н. Р.

Chocolate in Chocolate-Coated Tablets and Pills. E. S. Rose. (Amer. J. Pharm., 1924, 96, 590–592.)—Chocolate was detected by removing the coating from 3 to 10 tablets with warm water, slightly acidifying with acetic acid, boiling, adding 1 grm. of precipitated chalk, filtering, and washing with warm water. Five c.c. of 10 per cent. sodium carbonate solution were then added to the precipitate, which was boiled for 2 minutes, filtered off, and washed with 2 c.c. of water, the filtrate acidified with acetic acid, treated with 3 c.c. of copper sulphate solution (5 grms. copper sulphate, 1 c.c. glacial acetic acid, and 100 c.c. of water)

allowed to stand half-an-hour and centrifuged for 2 to 3 minutes. A brown flocculent precipitate indicates cocoa, and 5 mgrms. of cocoa may thus be detected if the mixture is allowed to stand several hours before centrifuging. Ferric oxide, burnt umber, extract of liquorice, coal-tar colours, chalk, cane sugar, glucose, gelatin, gum arabic, starch, etc., do not interfere. It was found that cocoa was present in less than half the brown-coated samples examined, the amount being probably less than 5 per cent. of the coating used. D. G. H.

Microchemical Detection of Acetaldehyde in Fruits. C. Griebel. (Zeitsch. Unters. Nahr. Genussm., 1924, 47, 438-441.)-Acetaldehyde, which has been shown to be present in apples and stone fruits, may be detected even in minute quantities microchemically by means of the characteristic crystals which it forms with p-nitrophenylhydrazine. A tiny fragment or section of the fruit is placed in a small cell formed by a piece of barometer tubing about 15 mm. long and a micro-slide; to it are added a minute crystal of the reagent and a drop of dilute acetic acid (15 per cent.), and the whole is very gently warmed with a cover slip over the top for about 30 seconds. Characteristic crystals of acetaldehyde-p-nitrophenylhydrazine are sublimed on to the cover slip, which may be examined under 100 magnifications. The crystals are small yellow needle-like prisms, frequently sabre-shaped. The test, as so applied, will detect as little as 0.002 mgrm. of acetaldehyde or, say, 0.05 per cent. in a fragment of fruit. Certain other aldehydes or ketones, such as acetone, benzaldehyde or furfuraldehyde, give a similar reaction, but the colour and shape of the crystals are different. H. E. C.

The Solanine Content of the 1922 Crop of Potatoes. C. Griebel. (Zeitsch. Unters. Nahr. Genussm., 1924, 47, 436-438.)—A serious outbreak of potato poisoning occurred in Germany in the autumn of 1922 which was traced to an abnormal amount of solanine in the potatoes raised in that year (cf. ANALYST, 1923, 48, 454). Some specimens contained as much as 0.79 per cent., as compared with a content of about 0.05 per cent. in the 1923 crop; this is attributed to the abnormally wet weather then prevailing, and, secondly, to the influence of light during storage or exposure for sale. Those tubers or parts exposed to the light contained much more solanine than other parts, so that, of the same potato, one part may be poisonous and another not so. (Cf. also ANALYST, 1924, 284.)

H. E. C.

Molecular Combination of Caffeine and Salicylic Acid. A. Regenbogen and N. Schoorl. (*Pharm. Weekblad*, 1924, 61, 34–36.)—Equimolecular weights of caffeine and salicylic acid, when fused together, form a compound termed caffeine-salicylic Acid. It can be crystallised from water or chloroform in the form of microscopic, dextro-rotatory crystals, m.pt. 137°. Evidence points to the fact that "Salicylas Natricus cum Caffeine" of the Netherlands Pharmacopoeia, known as caffeine-sodium salicylate, is in reality the sodium salt of the caffeinesalicylic acid obtained by the author. W.S.S. **Reaction of Antipyrine with Trichloracetic Acid. L. Debucquet.** (J. Pharm. Chim., 1924, 30, 121–122.)—Antipyrine and trichloracetic acid are dissolved in weights proportional to their molecular weights in equal volumes of water, the solutions mixed and vigorously shaken, and the resulting viscous mass and supernatant liquid allowed to crystallise for 2 or 3 days, when an opaque crystalline block will have formed. Re-crystallisation, with slow cooling, results in the formation of anhydrous shining plates melting at 79–80° C., easily soluble in alcohol, chloroform, ether and benzene; slightly soluble in petroleum spirit; giving acid solutions showing all the colour reactions of antipyrine with ferric chloride and sodium nitrite, and negative results with acidified silver nitrate solution. Owing to the instability of the solution the trichloracetic acid may be estimated directly with 0.1 N sodium hydroxide solution, and the antipyrine by Bougault's volumetric method, after eliminating the trichloracetic acid. Results obtained agreed with the formula  $CCl_3COOHC_{11}H_{12}N_2O$  and a molecular weight of 351.5. D. G. H.

**Commercial Anhydrous Quassine.** Rengniez. (J. Pharm. Chim., 1924, **30**, 120–121.)—Since the first process in the preparation of crystalline quassine produces a variable extractive termed "amorphous quassine," but differing entirely in properties from either crystalline, or the true amorphous quassine produced from the crystalline variety, and containing from rather less than one-tenth to over two-tenths of crystalline quassine, the author advocates the exclusion of such a varying product from the French Pharmocopoeia. D. G. H.

Detection of Diethyl Phthalate. H. Leffmann. (Amer. J. Pharm., 1924, 96, 503-505.)—Diethyl phthalate may be used as a denaturant for commercial alcohol, and a comparison of the methods used in its detection have shown that good results are obtained by Lyon's modification of Utz's method, in which 1 c.c. of the sample and 1 c.c. of concentrated sulphuric acid are heated together till the alcohol is driven off, slightly cooled, a pinch of resorcinol added and the mixture heated till it becomes reddish-brown, after which it is cooled, excess of ammonium hydroxide solution cautiously added, and the whole poured into 500 c.c. of water, when fluorescence will result if the phthalate was present. Andrews' method, however, (ANALYST, 1923, 48, 508) is particularly simple and dependable. Acetaldehyde, commercial methyl alcohol and commercial isopropyl alcohol in quantities likely to be present in recovered or imperfectly prepared alcohol were not found to interfere in Andrews' method. D. G. H.

## Biochemical, Bacteriological, etc.

Haemolysis, as a means of Detecting the Adulteration of Milk. M.J.N. Schuursma. (*Chem. Weekblad*, 1924, 365-367.)—Haemolysis has been found to take place in milk of a certain dilution, and a method, known as the "Erythrocyte method" was devised by the author for the detection of dilution of milk. It has an accuracy comparable with that of the usual method, and at the same time, requires a shorter time for the estimation. The method is as follows:--Preliminary experiments are carried out on a normal (undiluted) milk. Portions, each of 10 c.c., of the normal milk are pipetted into a number of dry test tubes, and distilled water, varying in amount from 1 c.c. upwards, added; 5 drops of fresh ox blood are added, the solution well mixed, and, after standing for 15 minutes, centrifuged for ar least 20 minutes. The dilution at which haemolysis begins is indicated by the first appearance of a red coloration in the supernatant liquid. The experiments are repeated, varying the dilution of the milk to approximate to the dilution already found to produce haemolysis, and thus an accurate estimation can be made. The milk to be tested, is now diluted in exactly the same manner, and the point at which haemolysis begins should correspond to that already determined in the blank. Dilution of the milk may be detected by the increase of haemolysis as compared with the blank. W. S. S.

Application of Permutit to the Separation and Estimation of Ammonia in Urine. A. Kolb. (Chem. Zeit., 1924, 48, 557.)-Folin and Bell (J. Biol. Chem., 1917, 29, No. 2) published a paper on the colorimetric estimation of ammonia in urine with synthetic zeolite (permutit). Permutit as prepared by Gans (Chem. Zeit., 1907, 355; Kolb, Chem. Zeit., 1911, 1393, 1410, 1419), after being subjected to special treatment, has been changed into a pure, moderately fine, insoluble powder, which, in contact with water, gives no dusty constituents, and settles quickly after being shaken with water. Basic ammonia contained in a liquid may be removed easily with permutit, and other organic, nitrogenous materials contained in urine are removed by being washed out from the permutit. The taking up of ammonia by permutit is an exchange of ions and not a case of absorption; through the action of another salt solution, e.g., sodium chloride solution, the base can be made free again. The new colorimetric method is described in detail. It is simple and quickly and easily carried out. After the ammonia has been freed by the addition of sodium hydroxide solution it is estimated colorimetrically in the usual way with Nessler's reagent. A large number of comparative estimations of ammonia in pathological urine gave corresponding values by the new colorimetric and the distillation methods, but the former was always more rapid. P. H. P.

Efficiency of some Organic Dyes as Anti-ferments. E. H. Harvey. (Amer. J. Pharm., 1924, 96, 585-589.)—Since yeast gradually hydrolyses dextrorotatory sucrose to equal parts of dextrose and laevulose, the reaction may be followed by the change in hourly polarimetric readings (ANALYST, 1923, 48, 131, 232), and the efficiency of anti-ferments will be inversely as the increase in the difference between readings. Of the dyes tested, safranine was found to be the most efficient anti-ferment, followed by paranitrophenol, methylene blue, eosin Y, aniline violet (methyl), cyanine and fuchsin, whilst alizarine blue had no antiferment effect. A table is given showing the relative efficiency on a percentage basis of the various anti-ferments tested on this and previous occasions, together with an extensive bibliography on the use of dyes as bactericides. D. G. H. Detection of Koch's Bacillus in Ordinary Media. G. Pégurier. (Ann. Chim. anal., 1924, 6, 226-229.)—A fragment of sputum is warmed on a slide with carbol-fuchsine solution, freed from excess of the stain, treated with an aqueous alcoholic solution of lactic and picric acids, washed with water, and with 95 per cent. alcohol until the yellow colour of the picric acid appears, and then counterstained with Esbach's aqueous citro-picric acid reagent. After removal of the excess of the stain, the Koch's bacilli, coloured scarlet, stand out clearly from the other bacteria and tissue elements, which appear saffron yellow. In most instances this procedure indicates a greater number of Koch's bacilli than are rendered evident by the Ziehl-Nielsen method. T. H. P.

Fermentation of Pentoses by Bacillus Granulobacter Pectinovorum. W. H. Peterson, E. B. Fred and E. G. Schmidt. (J. Biol. Chem., 1924, 60, 627-631.) -Speakman (J. Biol. Chem., 1923-24, 58, 395) has classified the carbohydrates into two groups, those which ferment normally and those which do not. Glucose and starch illustrate normal fermentation, in which the acidity reaches a maximum, falls rapidly, then slowly rises again. Xylose and arabinose he placed in the group producing abnormal fermentation; high acidities with little or no break in the curve were found with both pentoses. No quantitative data on solvent production are given by him. The authors find that the fermentation of xylose and arabinose by Bacillus granulobacter pectinovorum results in the same products and in essentially the same quantities as from glucose. Slightly less solvents and slightly more volatile acids are produced from the pentoses. The rate of fermentation is somewhat slower for the pentoses than for glucose; but practically all the sugar is destroyed in 72 hours. The destruction of sugar and production of solvents do not agree with Speakman's statement that abnormal fermentations (xylose, mannitol, etc.) are characterised by a low consumption of carbohydrates and a poor yield of solvents. P. H. P.

Determination of the Number of Bacteria in Soil. C. L. Whittles. (J. Agric. Sci., 1924, 14, 346-369.)—The author has shown in a previous paper (ANALYST, 1923, 48, 280) that the frequency of vibration has a profound influence on the disintegration of soil particles, and hence on the bacteriological count as obtained by plating out in the usual way. A new apparatus is now described by which the frequency may be varied at will and measured. The degree of disintegration following vibration, with and without shaking and trituration, has been measured by a modification of Robinson's depth concentration method (ANALYST, 1923, 48, 83). Vibration alone is not satisfactory, but should be preceded by trituration with a rubber-covered pestle. The rate of wetting is an important factor; the use of acids is not advisable, but ammonia may be used. H. E. C.

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## Toxicological and Forensic.

Distribution of Lead in the Living Organism. I. A. Christiansen, G. Hevesy and S. Lomholt. (Compt. rend., 1924, 179, 291-293.)—The determination of the distribution of lead in different organs of the body has been made by the radio-activity method already described for bismuth (*Biochem. J.*, 1923, 17, 441). It consists in administering lead containing a known amount of radium D, then estimating the lead in the different organs by decomposition with nitric acid, and measuring the equilibrium between the lead contained therein and the  $\beta$ -rays of radium E by means of an electroscope. The results show that the greater part of the lead accumulates in the liver, whence it is slowly eliminated in the fæces; considerable amounts are also found in the intestines and kidneys.

H. E. C.

Solubility of Various Lead Compounds in Blood Serum. L. T. Fairhall. [J. Biol. Chem., 1924, 60, 481-484.]—It is of fundamental interest to know how lead is absorbed from the mucous membranes and respiratory tract and transported in the circulation. This investigation was carried out to determine whether the solubility of lead compounds in the fluids of the tissues is different from that in pure water. Blood serum (horse serum) was used as a representative medium, and in it the solubilities of metallic lead and certain lead salts were determined. The solubilities were also determined in serum saturated with carbon dioxide. Experimental details and tables of results are given. No marked increase in solubility was noted with the serum except in the case of lead oxide. Whereas in water its solubility is 17 mgrms., in serum it is 1.15 grms. per litre. Lead oxide and lead fume, both being readily soluble in serum, would be expected to find an easy mode of entrance into the circulatory system by forming lead hydroxide and combining with protein to form an alkali metaprotein. The proportion of those suffering from lead encephalopathy is higher in the manufacture of lead oxides than in any other lead industry. Possibly the ready solubility of these compounds allows lead to enter the system more quickly than it can be eliminated or deposited in the bones as relatively harmless lead phosphate, and the large quantities circulating tend to produce severe lead poisoning. P. H. P.

Rapid Method of Testing Urine for Lead. L. T. Fairhall. (J. Biol. Chem., 1924, 60, 485–488.)—Obvious methods for the analysis of urine and the estimation of its lead content are discussed and shown to be unsatisfactory. The author has devised a method for the quantitative precipitation of lead from urine by mechanical precipitation with the earthy phosphates. If fresh or well preserved urine is made strongly ammoniacal, and the mixture left overnight at room temperature in a large Erlenmeyer flask, the alkaline earth phosphates precipitate in a gelatinous mass so completely that the clear liquid above can be decanted. The precipitate can then be rapidly separated by suction filtration, collected, ashed and the amount of lead present then estimated

volumetrically with greater facility than by the usual method of evaporating the urine to dryness and ashing the residue. Known amounts of lead were added to urine, in a series of experiments, before the addition of ammonia, and the recoveries were satisfactory. The method was applied to the urine of patients suffering from lead-poisoning, and results given show that the lead is all precipitated and the filtrate is lead-free. The urine must either be freshly collected or well preserved with powdered thymol, and heating should be avoided. P. H. P.

## Water Analysis.

Colorimetric Estimation of Lead and Copper in Water. C. Pyriki. (Zeitsch. anal. Chem., 1924, 64, 325–330.)—Winkler's sulphide method (Zeitsch. angew. Chem., 1913, 26, 38) for the estimation of lead and copper gave good results for lead up to 0.002 grm. per litre; the results for copper should be multiplied by 0.813, as copper sulphide has a stronger colouring power than lead sulphide. With larger quantities of lead the results were much too low; this was proved to be due to the cyanide added, which prevents quantitative conversion into lead sulphide, probably by the formation of lead cyanide; the interference is not removed by addition of the sulphide first and the cyanide afterwards. The method was quite satisfactory in absence of copper, no cyanide being required. Winkler's ferrocyanide and sulphide method (*loc. cit.*) for the simultaneous estimation of copper and lead was found to be trustworthy. W. R. S.

## Agricultural Analysis.

New Method for the Estimation of Cyanamide in its Calcium Compound. R. Fosse, P. Hagene and R. Dubois. (Comptes rend., 1924, 179, 408-410.)—When heated for 3 hours at 50° to 55° C. with 2N- or N-nitric acid, silver cyanamide yields quantitatively the corresponding amount of urea, the estimation of which then gives the cyanamide to within 0.5 per cent. With calcium cyanamide, 1 grm. of the material is mixed with 10 c.c. of water and 50 c.c. of 2N-nitric (or hydrochloric) acid in a conical beaker, which is immersed for 3 hours in a bath at  $50-55^{\circ}$  C. The liquid is then cooled, rendered slightly alkaline with ammonia, filtered, washed into a 500 c.c. flask and made up to volume with water. Of this solution 20 c.c. are treated with 40 c.c. of acetic acid and 3 c.c. of a 10 per cent. solution of xanthydrol in methyl alcohol for 3 hours, the xanthylurea being then collected, dried and weighed. The results thus obtained differ but slightly from those furnished by Caro's method.

T. H. P.

Colorimetric Estimation of Humic Matter in Mineral Soils. T. Eden. (J. Agric. Sci., 1924, 14, 469-472.)—The method, which is a modification of that of Oden, estimates the total coloured organic matter of the soil, and includes the so-called humic acid and humin. Five grms. of the soil are treated in a Gooch crucible with 50 c.c. of 10 per cent. hydrochloric acid and well washed. The soil

is then transferred, with the aid of about 60 c.c. of water, to a conical flask marked at 100 c.c., plus the volume of the soil, 20 c.c. of 50 per cent. sodium hydroxide solution are added, and the flask is filled to the mark (a few drops of alcohol may be used to clear the meniscus if necessary). It is then immersed in boiling water for 15 minutes and its contents constantly stirred. A portion of the hot solution is filtered through a hardened paper, and 10 c.c. of the filtrate are diluted to 200 c.c. and compared in a colorimeter with a standard solution of Merck's *acidum huminicum*, which may contain about 0.3 grm. of the dry material dissolved in a slight excess of sodium hydroxide solution and made up to 100 c.c. H. E. C.

Gravimetric Estimation of Cyanamide in the Form of Xanthyl-Urea. R. Fosse, P. Hagene and R. Dubois. (*Comptes rend.*, 1924, 179, 214-216.)— Pure silver cyanamide may be estimated easily and accurately in the form of dixanthyl-urea:—

$$O \underbrace{C_{e}H_{4}}_{C_{e}H_{4}}CH-NH-CO-NH-CH \underbrace{C_{e}H_{4}}_{C_{e}H_{4}}O.$$

Silver cyanamide in contact with nitric acid  $(40^{\circ} \text{ Bé.})$ , freed from nitrous vapours, is completely transformed into urea nitrate. The yield is theoretical if the mixture is left overnight at ordinary temperature or is kept for  $1\frac{1}{2}$  to 2 hours at  $38^{\circ}$  to  $40^{\circ}$  C. If left overnight, water is added next day to the crystalline mass thus formed in a stoppered bottle, the contents are made slightly alkaline with concentrated ammonium hydroxide, and treated with acetic acid and with a 10 per cent. solution of xanthydrol in methyl alcohol. After 2 hours of condensation the xanthyl-urea is washed with alcohol on a filter funnel, dried and weighed directly. Its weight, divided by 10, represents the corresponding amount of cyanamide, and by 7, the amount of urea formed. Two methods, varying slightly, carried out at ordinary temperature are described in detail, and two other similar ones carried out at  $38^{\circ}$  to  $40^{\circ}$  C. Results cited show the errors to be small.

Estimation of Uric Acid in Poultry Excreta. H. E. Woodman. (J. Agric. Sci., 1924, 14, 413-427.)—The well-known processes for the estimation of uric acid in urine are not applicable to its estimation in poultry excreta, and the piperidine extraction method is not altogether satisfactory. The new method proposed consists in the following stages: the removal of pigment, the decomposition of ammonium urate by hydrochloric acid, extraction of the uric acid by means of lithia, precipitation of the uric acid by ammonium chloride, decomposition with acid and titration with 0.05 N potassium permanganate solution. The method is applied as follows:—Eight to ten grms. of the mass are stirred with about 30 c.c. of alcohol, and the alcohol is poured off through a filter, this being repeated twice more with alcohol, then with ether. The extracted mass and the material on the filter paper are mixed with 35 c.c. of water, heated to boiling, after which 5 c.c. of hydrochloric acid are added, and the boiling is continued

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until the volume is reduced to about 20 c.c.; then the beaker is set aside in a cool place overnight. The acid liquor is poured through a filter, and the mass washed once with a little cold water. The material is now boiled with about 40 c.c. of water and 5 c.c. of 5 per cent. lithia solution. After settlement of the undissolved matter the solution is poured through a filter, and the residue is re-extracted with more dilute lithia solution. The filtrate and washings are evaporated to 100 c.c., then 30 grms. of ammonium chloride are stirred in and, next morning, the ammonium urate is filtered off and washed with ammonium chloride solution. The ammonium urate is dissolved in 50 c.c. of hot water and 5 c.c. of hydrochloric acid, from which, on cooling, the uric acid separates out; it may be collected on a Gooch filter, dried and weighed, or (preferably) dissolved in dilute lithia solution, acidified with sulphuric acid, and titrated hot with 0.05 N potassium permanganate solution.

## Organic Analysis.

Effects of varying Hydrogen Ion Concentration on Tannin Analysis. W. R. Atkin. (J. Soc. Leather Trades Chem., 1924, 8, 425.)—A summary is given of various papers on this subject with the author's comments. He points out that the variations in the tannin content of a natural quebracho extract (increasing from 61.6 per cent. to 72.6 per cent. over a range of  $P_{\mu}$  1.86 to 8.0) are caused by a decrease in the insolubles, the sum of tannin and insoluble remaining almost constant. In the case of mangrove the addition of hydrochloric acid, although increasing greatly the insolubles, appeared to convert some non-tannin into tannin, but with chestnut and oak extracts the addition of acid decreased the tans and increased the non-tans. Comparing the  $P_{\mu}$  of natural quebracho extract before and after detanning, the author quotes the figures 4.56 and 4.27respectively, whereas other workers find 4.60 and 5.57. The amounts of 0.1 Nsodium hydroxide solution required to bring the tannin solution to  $P_{\mu} = 7.0$ , as found by titration, failed to do so in actual practice, and he ascribes this to oxidation by air and subsequent reduction by the hydrogen electrode. It is pointed out that catechol tannins give distinct variation in results with the colorimetric, hydrogen electrode and quinhydrone electrode methods, whilst the pyrogallol tannins yield concordant results. R. F. I.

## Inorganic Analysis.

Benzidine as an Analytical Reagent and an Indicator for a definite Oxidation Potential. I. M. Kolthoff. (*Chem. Weekblad*, 1924, 21, 2-4.)—The colour change to bluish-violet undergone by benzidine acetate in the presence of oxidising agents, such as dichromates, etc., is made use of in the determination of a given oxidation potential. Particular attention is given to the oxidation potential of mixtures of ferricyanide and ferrocyanide. Ferricyanide was found to give the

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reaction readily, whereas attempts with ferrocyanide were negative. In the case of a mixture of the two it was found that the colour change, which is an indication of the oxidation potential, was dependent on the ratio of the two components of the mixture, but was independent of the absolute amounts present. Thus, when the ratio of ferricyanide to ferrocyanide was 9:1, a bluish-violet colour was obtained with benzidine acetate after one hour, but as the ratio decreased the intensity of the coloration diminished, till at 1:9 no colour was obtained. W. S. S.

Antimony Trichloride in Volumetric Analysis. F. Feigl and O. Schummer. (Zeitsch. anal. Chem., 1924, 64, 249-255.)—Antimony trichloride solutions are not oxidised by atmospheric oxygen, hence their reducing action remains constant. In the following volumetric methods the antimony solution is added in excess, which is subsequently measured by Györy's bromate titration; standardisation is effected against bromate. Hypochlorite. The reaction proceeds as follows:  $-NaOCl + SbCl_a + 2HCl = NaCl + H_2O + SbCl_5$ . A measured excess of antimony solution is added to the hypochlorite liquor; the mixture is treated with hydrochloric acid and well shaken to dissolve any basic antimony compounds. The reaction is instantaneous, and the bromate titration can be carried out at once. Chloride of lime. A thin paste, prepared by trituration, is diluted to a definite volume and an aliquot part treated as above. Ferricyanide. The reaction is  $2K_3Fe(CN)_6 + SbCl_3 + 4HCl = H_4Fe(CN)_6 + K_4Fe(CN)_6 + SbCl_5 + 2KCl$ . The measured excess of antimony solution is 'added to the ferricyanide solution, followed by treatment with strong hydrochloric acid and warming until the colour of the liquid changes from reddish-brown to nearly colourless. If the colour change is slow, more hydrochloric acid should be added. The liquid is then cooled, treated with excess of zinc sulphate solution free from iron, and titrated with bromate. Ferrocyanide can be estimated in the same manner after conversion into ferricyanide; the solution is acidified with sulphuric acid (1: 4) and oxidised with excess of permanganate; this is destroyed by careful addition of oxalic acid. Ferricyanide and ferrocyanide can be estimated in presence of each other by the above methods. W. R. S.

Titanous Salts as Reducing Agents. E. Knecht. (J. Chem. Soc., 1924, 125, 1537–1546.)—The quantitative reduction of nitric to nitrous acid in the presence of titanous chloride and an acceptor in the form of a primary aromatic amine can be conveniently utilised under certain conditions to diazotise the amine. Reduction of  $\alpha$ -nitronaphthalene with titanous chloride (5 per cent. in excess of the 4 molecules required to produce the mono-chloro compound) in the presence of hydrochloric acid (24 molecules) will produce a 94 per cent. yield of crude 4-chloro- $\alpha$ -naphthylamine, of melting point 94° C. Methods for the volumetric estimation of tetramethyldiaminobenzhydrol, phenolphthalein, gallein, alizarin S, tartrazine, isatin, and glucosazone by means of titanous chloride are described, and also for the accurate estimation of phenylhydrazine in the products of acid hydrolysis of glucosazone. D. G. H.

Estimation of Phosgene. H. G. Reeves. (J. Soc. Chem. Ind., 1924, 43, 279T.)—Two methods are given: (1) By passing the gas into 13 N sodium hydroxide solution, which decomposes it with formation of sodium chloride and separation of sodium carbonate, which are then both estimated; (2) by leading the gas through a heated combustion tube containing asbestos impregnated with pure zinc dust. After cooling, the zinc is washed out of the tube with dilute nitric acid, and the chlorine estimated by Volhard's method. Free chlorine as an impurity is readily estimated either by passing the gas through potassium iodide solution and titrating the liberated iodine with thiosulphate solution, or by shaking the impure gas with mercury in a bulb immersed in a freezing mixture, the gain in weight of the mercury after gasification of the phosgene indicating the amount of chlorine present. Free hydrochloric acid is best estimated by passing the adulterated gas first of all through a cold U-tube containing glass wool coated with pure zinc dust. This combines with the hydrochloric acid, but not with the phosgene. The zinc chloride formed is estimated as before, and the phosgene by methods 1 or 2 above. Phosgene can be readily concentrated and kept for examination by passing it through nitrobenzene, which absorbs large volumes of the gas at ordinary temperatures and immediately gives it off again on heating the solution on a water bath till gas evolution ceases. Total removal of the gas is then effected by passing a current of dry air through the heated solution. R. F. I.

The Thiosulphate Precipitation of Copper. Drawe. (Chem. Zeit., 1924, 48, 593.)—After the precipitation of copper sulphide by means of thiosulphate, the filtrate, if required for the estimation of other metals, must be subjected to evaporation and oxidation for the purpose of destroying the excess of precipitant. These manipulations can be obviated by adding a slight excess of sodium carbonate, precipitating the metals by addition of sodium sulphide, and dissolving the sulphide precipitate in hydrochloric acid. W. R. S.

Oxidation of Arsenious Acid in Alkaline Solution by Permanganate. F. Feigl and F. Weiner. (Zeitsch. anal. Chem., 1924, 64, 302–322.)—A critical study was made of this reaction, which is stated to take place according to  $3A_{s_2O_3}+4KMnO_4=3A_{s_2O_5}+2K_{2O}+4MnO_2$ . The authors find that the equation is correct only in presence of a constant excess of permanganate; they condemn as unreliable the methods of Reichard for the estimation of permanganate (and of lead peroxide) by means of alkaline arsenite solution, it being found that the manganese peroxide formed, as well as atmospheric oxygen, contributes to the oxidation of the arsenite. Reichard's methods should be excised from the textbooks (e.g. Rüdisüle, Vol. V., 462; Classen, *Theorie und Praxis der Massanalyse*, 411–412). Brauner's statement (*Zeitsch. anal. Chem.*, 1916, 55, 225) that manganese sesquioxide is the product of the reaction could not be confirmed; the precipitate was found to be richer in oxygen than  $Mn_2O_3$ . W. R. S. Use of Molybdenum as Indicator in the Volumetric Estimation of Zinc. L. Fernandes. (Giorn. Chim. Ind. Appl., 1924, 6, 334-335.)—Since, in acetic acid solution, alkali molybdates are not precipitated by potassium ferrocyanide, but give an intense red coloration, they serve as indicators in the estimation of zinc by titration with ferrocyanide, rendering the end-point more distinct, and thus diminishing the comparatively large error to which this method is subject. The zinc solution is evaporated to about 25 c.c., neutralised with ammonia, if containing mineral acid, or with acetic acid if alkaline, treated with 10 c.c. of glacial acetic acid and 2 c.c. of 30 per cent. ammonium molybdate solution, and titrated with standard potassium ferrocyanide solution until a persistent yellowish-pink coloration forms.

In the case of a zinc ore, 1.5 grms. of the finely powdered material are treated in a roomy dish with 20 c.c. of aqua regia, evaporated to dryness, and the dry residue mixed with 15 c.c. of concentrated hydrochloric acid and evaporated to dryness to render the silica insoluble. The residue is boiled with 5 c.c. of hydrochloric acid and 5 c.c. of water, and the liquid then diluted with 200 c.c. of water, treated with hydrogen sulphide to precipitate the heavy metals, and filtered into a large beaker. The excess of hydrogen sulphide is expelled by boiling, the solution boiled with a few drops of nitric acid and then treated with ammonia, ammonium carbonate and a small quantity of hydrogen peroxide. The precipitate is filtered off, washed into a 500 c.c. flask and redissolved in boiling dilute hydrochloric acid, the solution then evaporated to expel most of the acid, and the residue, dissolved in water, and the solution treated, drop by drop, with ammonia until precipitation is complete. Both liquid and precipitate are introduced into the 500 c.c. flask containing the previous solution, and the whole cooled and made up to the mark. After filtration 100 c.c. are evaporated to about 25 c.c., and the procedure described above then followed. T. H. P.

Electrometric Titration of Chromic Acid. H. T. S. Britton. (J. Chem. Soc., 1924, 125, 1572-1582.)-It has been found possible to titrate chromic acid electrometrically provided that certain precautions are taken. The electrode must be of platinum foil, not wire, should contain lead and be coated with platinum black, and should be immersed completely in the perfectly still solution. It is, however, not easy to obtain concordant results, so that an oxygen electrode is preferable, this being standardised against the hydrogen one. The course of the neutralisation curve shows that there are two stages-the formation of sodium hydrogen chromate, then the extremely weakly dissociated anion  $HCrO'_4$ , which is neutralised to form sodium chromate. The dissociation constant of  $HCrO_4$  is  $4.4 \times 10^{-7}$  at  $18^{\circ}$  C., whereas  $H_2CrO_4$  is almost completely dissociated. For the titration with an oxygen electrode the chromic acid solution are connected through a bridge with saturated potassium chloride and a normal calomel cell, and the P.D. between it and the electrode is measured potentiometrically in the usual way. The E.M.F. obtained is more steady when oxygen is passed through at a fairly uniform rate of about 5 bubbles per second. H. E. C.

Colour Reaction for the Detection of Zirconium and Fluorine. J. H. de Boer. (*Chem. Weekblad*, 1924, 21, 404-405.)—Many metals, under given conditions, yield colour reactions with alizarine sulphonic acid, but it was found that, in the presence of a very large excess of concentrated hydrochloric acid only the yellow colour due to zirconium persisted. It was possible by means of this reaction to detect 0.02 mgrm. of zirconium per c.c. The change to the yellow colour is effected particularly rapidly in the presence of small quantities of fluorine ions. By mixing 2 c.c. of a zirconium solution containing 0.01 grm. zirconium per c.c. with 5 c.c. of an alizarine sulphonic acid containing 0.003 grm. per c.c., and adding 60 c.c. of concentrated hydrochloric acid, a reagent is obtained capable of detecting 0.001 mgrm. of fluorine in 1 c.c. water, whilst, if double the amount of concentrated hydrochloric acid is used, the sensitiveness of the reaction is increased ten-fold. W. S. S.

Microchemical Estimation of Perchlorate. A. Pamfilov and W. Jofinow. (Chem. Zeit., 1924, 94, 541.)—The solution under examination is treated with solid sodium bicarbonate till just alkaline; 3 to 4 drops are placed on a slide, treated with 10 to 15 small crystals of rubidium chloride and dried carefully but completely over a flame. The crystalline mass is almost dissolved in 1 or 2 drops of weak potassium permanganate solution and the liquid evaporated till crystals begin to form on the circumference. The subsequent crystallisation is observed under the microscope. The development of isomorphous rose-coloured rhombic crystals denotes the presence of perchlorate. These are easily distinguished from the small deep coloured crystals of permanganate, which, as a rule, are absent in the presence of perchlorate if the permanganate solution has been weak enough. This method makes possible the detection and, with practice, an approximate estimation of perchlorate in solutions of 0.1 per cent. strength. It is more delicate than the Klobbie-Visser method, because of the greater solubility of the potassium perchlorate crystals. It can be used successfully in the presence of considerable proportions of chloride and chlorate. R. F. I.

## Physical Methods, Apparatus, etc.

A simple Non-splash Ring for use with Scheibler's Desiccator. S. C. Bradford. (*J. Chem. Soc.*, 1924, 125, 1546.)—This consists of a bell-shaped ring to rest, narrow end downwards, on the constriction of the acid reservoir.

D. G. H.

## Reviews.

THE SIMPLE CARBOHYDRATES AND THE GLUCOSIDES. BY E. FRANKLAND ARMSTRONG, D.Sc., Ph.D., F.R.S., F.I.C. (Monographs on Biochemistry, edited by Dr. R. H. A. Plimmer and Dr. F. Gowland Hopkins.) Fourth Edition. Pp. xii.+293. London: Longmans, Green & Co. 1924. Price 16s. net.

The present edition of this work, which is larger than its predecessor (ANALYST, 1919, 44, 427) by over fifty pages, bears abundant evidence of the rapid progress

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in our knowledge of the carbohydrates and their derivatives during the past five years. The enlargement of the book is almost entirely due to the amplifications and additions rendered necessary by recent research.

Dr. Armstrong devotes a considerable amount of attention to the active forms of the hexoses now frequently referred to as the  $\gamma$ -forms, which appear to be of the utmost importance from the biochemical point of view. The constitution of these isomerides is still in question. Thus  $\gamma$ -glucose, until recently considered to contain a 1:2 ethylene oxide ring, is now thought to contain a propylene oxide ring. It is much more reactive than the well-known butylene oxide ( $\alpha$ - and  $\beta$ -) forms of glucose, and it has been suggested that the occurrence of an excess of sugar in the blood in cases of diabetes is due to failure to convert the comparatively inert butylene oxide form into the active  $\gamma$ -form. The active or  $\gamma$ -form of fructose is provisionally regarded as containing an amylene oxide ring; this form of fructose is perhaps present in sucrose.

A comparison of the chapter on the disaccharides (Chap. V.) with the corresponding chapter in the preceding edition illustrates recent progress in the chemistry of the sugars in a very striking manner. The work of Irvine and his collaborators on the methyl derivatives of the sugars has continued to bear remarkable fruit. Thus, in the cases of maltose, cellose and gentiobiose and the trisaccharide, raffinose, the nature of the union of the hexose residues has been elucidated.

The still more formidable problems involved in the investigation of the constitution of the polysaccharides are dealt with in a chapter which is a new feature of this edition. Here, again, the record is one of rapid advance, an advance which is largely owing to the work of the Purdie-Irvine school. It is interesting to note that inulin, which yields fructose only on hydrolysis, is derived from the  $\gamma$ -form of this sugar.

The present edition maintains the very high standard of the earlier ones, and Dr. Armstrong is to be congratulated on the discrimination shown in his selection of the new material now incorporated in the book. LEWIS EYNON.

INKS: THEIR COMPOSITION AND MANUFACTURE. 3rd Edition. By C. AINSWORTH MITCHELL, M.A., F.I.C., and T. C. HEPWORTH. Pp. xvi. +336. London: Charles Griffin & Co., Ltd. Price 12s. 6d. net.

Although the use of ink is almost universal and the amount consumed considerable, yet any intimate knowledge of it is very uncommon and, from the manner in which it is generally referred to, it might be thought that ink is always a fluid which is used only for writing, usually of a black colour, though occasionally red, and always of approximately the same composition. A reference to the table of contents of the book under review is sufficient to correct any such idea, and it is seen that ink may be in a state of powder, paste or liquid, and of almost any colour and composition, and that it is employed not only for writing, but also for printing and marking. An account therefore of the history, uses, modes of manufacture, properties, and methods of testing of the various kinds of ink, written by a specialist, must needs be both interesting and valuable. That this is so is proved by the fact that the present is the third edition, the first having been

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published in 1904. The present edition, which embodies all the latest knowledge on the subject of inks, is an enlargement and revision of the earlier work, and every section has been brought thoroughly up to date.

The book, which opens with a short historical introduction, is divided into three sections, namely, Writing Inks, Printing Inks and Inks for Miscellaneous Purposes respectively, the latter including Copying Inks, Marking Inks, Safety Inks, Sympathetic Inks, Ink Powders and Tablets, Stencil Inks, Machine-ruling Inks, Inks for Rubber Stamps, Inks for Typewriters, Waterproof and Fireproof Inks, and Inks for Writing on Glass, Metal, Wood, Leather, and Ivory. The book concludes with a Bibliography, a List of English Patents for Inks, extending from 1688 to 1923, and an excellent Index.

The book will prove invaluable to the manufacturer, who desires for his product satisfactory quality and uniformity of composition; to the analyst who may be called upon to test supplies of the raw materials or of finished inks in order to ascertain whether they conform to specification requirements, whether they are worth the price asked and whether they are suitable for the purpose required; to the specialist who wishes to prove the kind or date of an ink on a document suspected to be forged and to the users of the many different kinds of ink enumerated.

While all sections of the book should appeal to chemists, those that will prove most useful are the ones dealing with the chemical composition and methods of examination of the raw materials (including a very complete account of the different tannins, their nature, properties and methods of estimation), the nature of the compounds formed during the manufacture of iron-gall ink and the changes which occur on keeping, the composition and tests for the various colouring matters, particularly the organic ones, employed for making coloured inks, and the chemical examination of ordinary writing ink, both in bulk and also in the form of writing on a document.

Throughout the book there will be found evidence that it is no mere compilation of the work of others, but that it incorporates the results of much practical knowledge and original research on the part of the senior author, who is responsible for the chemistry. The reviewer from personal experience can bear testimony to the value of the book.

One is accustomed to find the books produced by this firm of publishers very well printed on good paper and with excellent reproductions of the illustrations, and the present volume forms no exception to the rule. A. Lucas.

OLII E GRASSI. VEGETALI, ANIMALI E MINERALI. 2nd Edition. By G. FABRIS. Pp. 671. Milan: U. Hoepli. 1923. Price 24 lire.

This is one of the useful little volumes in the series of industrial manuals which this leading firm of Italian publishers has been producing for some years, and the name of its author is well known as that of an authority on the chemistry of oils and fats.

The arrangement of the book is similar to that of the last edition, the first section dealing with vegetable oils, the second with animal oils, and the third

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with mineral oils. In each case the methods of extraction and purification of the respective oils and their composition and examination are discussed, and tables of the principal analytical values of 470 different fatty oils and fats, occupying 55 pages of the book, are included.

A good but brief outline of the methods of fat analysis is given, although this needs supplementing in some places. It is interesting to note that, according to the author (p. 182), Hübl's method of estimating the iodine value is still the one most generally used in Italy.

On p. 187 the measurement of heat of bromination as a rapid analytical test is attributed to Marden (1916). The reviewer has for years been under the impression that the test was devised by Hehner and Mitchell, and that it was first published in THE ANALYST.

For English chemists the most valuable portions of the work are the descriptions of the methods and plant now used in Italy for the production of olive oil, and the statistics of the Italian oil industry. The book concludes with a fairly full bibliography, but lacks an index. The classified table of contents can hardly be regarded as an efficient substitute for one. EDITOR.

PERFUMES AND SYNTHETICS WITH ESPECIAL REFERENCE TO SYNTHETICS. By W. A. POUCHER. Pp. xi. +462. London: Chapman & Hall, Ltd. 1923. Price 21s.

Of the more recent books on perfumery and allied subjects this is certainly one of the best; indeed, a perusal of the preface renders criticism difficult. The division of the subject matter into parts has strengthened the book in many ways. The first part is somewhat scrappy, but fairly comprehensive, though the absence of chemical formulæ indicative of the constitution of the various synthetic odorous substances is a matter for regret. The synthetic esters would have been better dealt with had the physical and chemical data been included in the descriptions of their properties; after all, it *is* chemistry that is concerned with their manufacture, and, alas, their adulteration, and every user of them, sooner or later, needs exact chemical knowledge of their composition.

An admirable feature of the book is the photographic illustration of processes and plant, though here, again, details of stills and the like might have been given in the form of a working drawing, rather than merely as a picture. A few of the pictures seem familiar.

The chapter on "Fixation" may be singled out as one of the best in the book, and the author is to be congratulated on this lucid and practical account of a very important branch of the perfumer's art. The monographs on floral perfumes are altogether too brief and should, in the writer's opinion, have been enlarged so as to aid the chemist who may have to examine such costly substances; really, though it may appear ungracious to say so, legend might have given place to practical details.

The pages relative to compounding preparations are full of good things, and the information is on the whole reliable and, in the main, modern. The style of the volume is excellent, and publisher and author alike must be congratulated on the production of a book which must be in the library of everyone interested in this subject. L. G. RADCLIFFE.